AN INTRODUCTION TO SURFACE CHEMISTRY

By

ERIC KEIGHTLEY RIDEAL
HUMPHREY OWEN JONES LECTURER IN PHYSICAL CHEMISTRY
CAMBRIDGE UNIVERSITY

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Wilt Thou not ope the heart to know
What rainbows teach and sunsets show?

EMERSON.

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PREFACE

By Professor F. G. DONNAN

THE importance of an accurate study of the actions, equilibria, and structnres which occur at the interfaces between homogeneous phases of matter is widely recognised at the present time. Thus a knowledge of these matters is required for a proper understanding of adsorption, the formation and stability of disperse or micro-heterogeneous systems (colloid sols and gels), catalysis, enzyme actions, etc., whilst the progress of research shows more and more clearly that the phenomena of life, i.e. the behaviour of cells and tissues, are intimately concerned with the actions occurring at surfaces, and that the effects produced by drugs, disinfectants, and other substances which profoundly affect the operation of cells and micro-organisms are largely due to surface actions.

From the general statistical and thermodynamic point of view, the scientific theory of surface phenomena was placed on a satisfactory basis by the researches of J. Willard Gibbs, Sir J. J. Thomson, and J. D. van der Waals. In comparatively recent times the more intimate molecular study of the structures and kinetics of surfaces has advanced very rapidly, thanks more especially to the pioneer work of Lord Rayleigh, André Marcelin, Sir W. B. Hardy and Irving Langmuir. Our knowledge of this subject has been greatly increased during the last few years by the excellent work of N. Adam and of E. K. Rideal. The combined effect of these researches has been to reveal the existence of a newly recognised so-called "two dimensional" molecular world, the dynamics of which is analogous to that of the ordinary "three dimensional" molecular world of homogeneous phases in bulk, whilst the structure of this "surface world" presents new phenomena of molecular orientation of the highest importance for the understanding of great regions of natural phenomena. The great merit of Dr E. K. Rideal's book lies in the fact that the author, whilst in no wise neglecting the thermodynamic treatment and its results, gives a very admirable account of this more recent and extremely important field of study.

Since this is also the most promising line of advance in the investigation of disperse systems, Dr Rideal's book can be most warmly recommended to all who are interested in colloid physics and chemistry. In the last two chapters the author gives a good introduction to the principal facts and theories of what is usually understood to-day as colloid chemistry, so that the reader is fully supplied with everything that is necessary for a thorough understanding of this subject. Every student and investigator of surface and colloid phenomena owes Dr Rideal a warm debt of gratitude for his admirable survey and presentation of a great and rapidly advancing field of physico-chemical science.

F. G. D.

UNIVERSITY COLLEGE,
LONDON.
April, 1926.

INTRODUCTION

THE essential differences between the properties of matter when in bulk and in the colloidal state were first described by Thomas Graham. The study of colloid chemistry involves a consideration of the form and behaviour of a new phase, the interfacial phase, possessing unique properties. In many systems reactions both physical and chemical are observed which may be attributed to both bulk and interfacial phases. Thus for a proper understanding of colloidal behaviour a knowledge of the properties of surfaces and reactions at interfaces is evidently desirable.

Whilst the conditions of equilibrium for such systems were clearly enunciated by J. Willard Gibbs and Sir J. J. Thomson a great impetus was given to the subject by supplementing the formal thermodynamic treatment with a clearer visualisation of the molecular structure of surfaces by Sir W. B. Hardy and I. Langmuir.

In this monograph an attempt has been made to present the subject from this point of view, and whilst the text is admittedly incomplete as a compendium on colloid chemistry yet it is hoped that the elaboration of the physics and chemistry of these degraded two-dimensional systems may prove of value to those concerned in problems of colloidal behaviour.

I wish to thank Professor F. G. Donnan for his stimulating interest, and to express my gratitude for the great assistance given me by Mr M. T. Sampson, Mr R. K. Schofield and Mr A. P. Cary who have been engaged in investigations on the properties of surfaces in this laboratory. But for their interest and labour this book would never have been planned and written.

ERIC K. RIDEAL

LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.
April, 1926.

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CHAPTER I

THE SURFACE TENSION OF LIQUIDS

1. The existence of surface phases.

It has been found that where one distinct phase adjoins another there exist conditions which distinguish the behaviour of a thin layer of matter at the boundary from that of the general mass in either of the homogeneous phases which bound it. Under certain circumstances at least, and perhaps always, the boundary is not simply a geometrical surface upon one side of which there is one phase of uniform properties and on the other a second phase, everywhere distinct from the first and homogeneous in itself: nor, again, do the contiguous phases shade, as might equally well be supposed, rapidly but continuonsly one into the other, so that the boundary would have to be considered as a more or less arbitrary mathematical definition rather than a physical entity: it lies in a film or lamina of finite though minute thickness consisting of an entirely new phase of definite and measurable properties. To this phase our attention will be given in the following pages. It will be seen that two of its dimensions may be varied at will like those of a phase in bulk, while its third dimension, which lies at right angles to the plane of the lamina is fixed: if in any way it be altered, a new superficial phase is formed.

A number of different types of such interfacial phases must be considered when dealing with bulk phases in their different physical states. Of special importance are the interfaces formed by contact of a bulk liquid with gaseous, liquid and solid phases whilst the problems connected with heterogeneous catalysis necessitate an examination of the properties of the solid-gas interface.

The mathematical treatment of surfaces was developed much earlier than the direct examination of superficial films. It is based primarily upon the observed tendency of a volume of liquid to adopt when unconstrained a shape with a minimum surface. The property of having a minimum surface for a given volume is possessed by a sphere, and this shape is assumed by a free body of liqnid. A falling raindrop is spherical: upon this fact indeed is based the

theory of the rainbow. In Plateau's beautiful experiment a drop of oil is formed in an aqueous solution of the same density by means of a tube dipping below the surface. The drop grows to any desired size, and when detached from the tube and floating without influence of gravity, it assumes a spherical shape. If distorted it will vibrate about its spherical figure of equilibrium. Upon any sufficiently small drop the influence of gravity, which increases with the cube of the radius, becomes negligible in comparison with the surface forces which depend on the square of the linear dimensions, so that dew-drops on spiders' webs or beads of liquid on the leaves of plants are almost spherical. If the surface is partly constrained it will adopt the least superficial area consistent with the constraint. This fact may be well illustrated by stretching a soap-film on a wire frame-work. A loop of cotton may be laid on the film, which is then broken within the loop; the outer part of the film drags out the cotton until its shape is circular and the film area has thereby become a minimum. By using several cotton threads knotted together we may vary this experiment as we please, always obtaining a figure of minimum surfaces. This fact has been applied practically to the design of structures.

A liquid thus behaves rather as if it were surrounded by an elastic skin with a tendency to contract. In a soap-film the force of contraction may be measured directly by suspending from a balance-pan a light square framework hanging in a vertical plane so that the lower horizontal bar is immersed in a soap solution and the part between the surface and the upper bar is covered with a film. The film tends to contract by pulling down the balance-pan. The pull is proportional to the horizontal length of the film: it is found under ordinary conditions to be about 23 dynes/cm. for each side of the film. The quantity thus measured is named the surface tension and may be defined as the force exerted on a straight line of unit length in the surface, in a direction parallel to the surface but perpendicular to the line. Imagining the length of the line and its proportional tension to diminish indefinitely, we arrive in the limit to the conception of surface tension at a point on the surface. The quantity, surface tension, will be denoted by the symbol σ. The usual unit is one dyne per cm.: in older works however one mgm. weight per mm. is used, a unit 9·81 times as great.

Surface tension is thus exactly analogous to pressure in three limensions except that the sign is reversed. By taking into considera-;ion the thickness of the surface film we can imagine surface tension is a negative pressure, averaged over the thickness of the film but it s seldom convenient to do so, partly because the thickness of the ilm is not usually known with certainty, and partly because the :alculated mean pressure has no very clear physical significance. We may however, if we choose, regard the surface tension as an ntegrated value of the tangential pressure over the thickness of he film.

There is another point of view from which it is often useful to egard surface phenomena. If the surface of a soap-film in a wire rame is increased by moving outwards against the tension one side of the frame, a quantity of work must be done against the surface ension equal to the product of the surface tension and the increase of area. A definite quantity of potential energy is thus bound up with each unit of surface. The numerical value of the surface nergy defined as energy per unit surface is clearly the same as hat of the surface tension. The dimensions in each case are $\frac{[\text{Mass}]}{[\text{Time}]^2}$. Since the potential energy of the system tends to a ninimum, the surface must contract to a minimum area: we are hus led to the same result as before.

It is important to observe that the surface energy σ is a quantity of the kind called "free energy" by Gibbs, and Helmholtz. It does not represent the whole of the energy expended when a fresh urface is formed. If the extension of surface takes place adiabati-ally, a quantity of heat $-T\frac{d\sigma}{dT}$, is absorbed from the interior, which s thereby somewhat cooled. Allowing for the additional energy, which may be called the latent heat of surface formation, introduced to compensate for this cooling effect, the total energy per unit of resh surface is $\sigma - T\frac{d\sigma}{dT}$: this quantity is known at the *Total Sur-ace Energy*: (u). We are as a rule more concerned with the free urface energy, and the latter quantity will be understood when for hortness the term surface energy is used.

2. The surface energy of liquids.

In the previous section we have noted that in the formation of an interfacial phase energy must be expended and that the free surface energy of an interface is related to the total surface energy by the Gibbs-Helmholtz equation

$$\sigma - u = T\frac{d\sigma}{dT},$$

thus the total interfacial energy may be determined from measurements of the free surface energy and the temperature coefficient of this quantity. Whilst computation of the surface energy for interfaces between solids and liquids or gases is a difficult matter; in the case where both the bulk phases are mobile such as at liquid-gas or liquid-liquid interfaces the value of the interfacial surface tension or free surface energy is readily determined.

The methods of measurement of the surface energy of liquids may be divided into two classes the static and dynamic methods. In general for pure unassociated liquids in contact with their vapour alone the values of the surface energy determined by the two methods do not differ beyond the range which may be attributed to experimental error. In other cases, however, marked divergence between the values obtained by the two methods is to be noted. This divergence is, as we shall have occasion to note, due to the comparatively slow rate of attainment by diffusion of equilibrium in the surface phase of solutions.

The static methods include the following:

(1) The rise or fall of liquid in a capillary tube or between plates inclined at a small angle.

(2) The weight of drops falling from a circular tube.

(3) The maximum pressure within a bubble of gas in the liquid.

(4) The measurement of the dimensions of curved liquid surfaces or bubbles.

(5) The direct pull of a soap-film, or ring from off the surface of a liquid.

(6) Langmuir's differential method for thin insoluble films on liquid surfaces.

Whilst the dynamic methods include

(7) The ripple method.

(8) Vibrating jets of fluid.

(9) Vibrating drops.

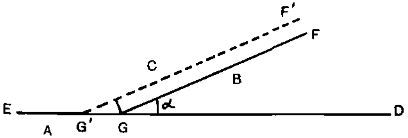
(10) Rate of flow of liquids in capillary tubes.

These methods are capable both of endless variations to suit any particular set of circumstances and of numerous modifications limited only by the ingenuity of the experimenter.

3. The angle of contact.

Whilst certain of these methods involve measurements only at the liquid-vapour or liquid-liquid interfaces involved; in the static methods we must usually consider besides the interfacial energy of the two fluids, that between each of them and a solid

There is at present no means of measuring satisfactorily the energy at any solid surface but the two energies of this kind may be eliminated from the calculation by taking into consideration the "angle of contact," in the following manner (Poynting and Thomson, *Properties of Matter*, p. 139).



Let A represent the solid, B, C the two fluids, EG, GD, GF the two solid-fluid and the fluid-fluid interfaces respectively, the line GF forming an angle α with ED. This angle is called the angle of contact of the system. Then since FG represents an equilibrium configuration the potential energy of the system in this position must be a minimum, so that an infinitesimal displacement of GF to $G'F'$ will not cause an alteration in the energy of the system.

If σ_{AC}, σ_{BC}, σ_{AB} be the respective interfacial surface tensions the total increase in energy will be

$$\delta A\sigma_{AB} + \delta A\sigma_{BC}\cos\alpha - \delta A\sigma_{AC},$$

where δA is the increase in area of the solid now in contact with B instead of with C, but this total energy change is zero, hence

$$\sigma_{AC} - \sigma_{AB} = \sigma_{BC}\cos\alpha.$$

Hence the difference between the tensions at the two solid-fluid interfaces which is the quantity always involved in equations of equilibrium can be expressed in terms of the fluid-fluid tension and an angle, called the angle of contact which is plainly susceptible of direct measurement.

The determination of this angle involves a certain amount of difficulty and very different results have been obtained by different observers for the angle of contact between the same pair of fluids at a given solid surface. The results have been found to differ according to whether the fluid has been in previous contact with the solid and the length of time during which contact has occurred. Thus Quincke found the angle of contact of mercury-air on a glass plate to be initially 148° 55′ but this value fell after two days to 137° 14′. Ablett investigated the angle of contact between water and a horizontally revolving cylinder of wax half immersed in the liquid. With the drum at rest α was found to be 104° 34′ ± 5′ at 10·4° C. When the drum was rotated at speeds of 0·44 mm. per sec. or greater so as to bring an unwetted part of the paraffin in contact with the water α was found to be 113° 9′ ± 5′, on reversal of the rotation so that the wet wax moved upwards out of the surface α was 96° 20′ ± 5′. The mean of the two latter angles is 104° 44′ which agrees within limits of error with the value for the cylinder at rest. As the velocity of rotation became less than 0·44 mm./sec. the difference between the extreme angles diminished but the mean remained the same as before.

If these results are compared with the equation

$$\sigma_{AC} - \sigma_{AB} = \sigma_{BC}\cos\alpha,$$

it follows that $\sigma_{\text{wax-air}}$ must be greater for wet wax than for dry since the surface tensions water-air and water-wax remain unaltered. The increase of surface tension of the wax-air interface on wetting is $\sigma_{BC}(\cos\alpha_1 - \cos\alpha_2)$. Taking σ_{H_2O} as 74·3 dynes per cm. we obtain

a value of 21 dynes per cm. This is the increase of surface energy owing to adsorption of water by wax. As we shall have occasion to note a water surface will hold hydroxyl groups of alcohols quite firmly but will exert little attraction for hydrocarbons, thus we may assume that the surface of the wax employed by Ablett contained a certain number of hydroxyl groups to which the water would adhere *.

For liquids which wet solids the angle is very nearly zero and may be taken as actually equal to zero without serious error. For ready determination of contact angles it is convenient to nse surface tension measurements by two methods of which, one depends upon, and the other is independent of the angle of contact. Such a pair of methods is the capillary rise and the bubble pressure method. If the surface tensions as calculated by these two methods agree to within one part in 500 it may be concluded that $\sin \theta < \frac{1}{500}$ or $\theta < 7'$ of arc. This is true of most pure wetting liquids for which accurate values of σ by two such methods are available. By various direct measurement methods Magie (*Phil. Mag.* XXVI. 150, 1888), Langmuir (*Trans. Farad. Soc.* XV. 62, 1920), Anderson and Bowen (*Phil. Mag.* XXXI. 143, 285, 1916) and Richards and Carver (*J.A.C.S.* XLIII. 827, 1921) have likewise concluded that the angle of contact is zero under these conditions.

A contact angle of zero or 180° implies that the liquid or gaseous surface is asymptotic to the solid at contact. In a capillary tube a liquid with zero angle of contact must therefore wet the tube to some distance above the visible meniscus. It is an experimental fact that unless care be taken to observe this condition erratic values for σ are obtained, no doubt because then the angle of contact does not vanish. A liquid with an angle of contact of 180° should similarly fail to wet a containing tube until well below the meniscus: the column of liquid will then be shielded by a gas film from the glass tube until this film is squeezed out by the hydrostatic pressure of the column. A zero contact angle between a given liquid and solid is equivalent therefore to the spreading of the liquid over the solid in presence of the gaseous phase present.

In the following pages a brief description of the more important methods employed for the accurate determination of the surface tensions of liquids is given.

* See also N. K. Adam and G. Jessop, *J.C.S.* CXXVII. 1863, 1925.

4. The capillary rise method.

Of the methods of measuring surface tension that depending on the rise of liquid in a capillary tube has been more widely used than any, with the possible exception of the drop-weight method. This is because, of all the static methods, of methods, that is, which give an equilibrium value for the surface tension, the conditions are the most clearly defined, and the calculations based upon them have a greater degree of certainty. It can be used equally at high and at very low temperatures: by this means Ramsay carried out determinations of the surface tension of organic liquids up to their critical points, and Kammerlingh Onnes that of hydrogen almost to its freezing point.

When a glass capillary tube is dipped into water the liquid rises in the tube above the general level of the water to a height which is approximately in inverse proportion to the radius of the tube. We may explain this event somewhat as follows: Water wets glass; it tends, that is, to spread over its surface and displace therefrom the air. In order that this may occur the sum of the surface energies involved must be reduced, and if nothing hinders (that is if the contact angle be zero), the water will continue to spread until all the glass is covered or all the water has been used to form a thin continuous film. When a vertical tube provides the surface over which the water must spread we have however a balancing tendency due to the effect of gravity on the water raised up in the tube. If the tube is narrow enough the rise of level is easy to calculate from the principle of virtual work. Let σ_1, σ_2, $\sigma_{1\cdot 2}$ represent the surface tension of water-air, glass-air and glass-water respectively. Imagine an infinitesimal rise of the liquid in the tube above its equilibrium position, without change of shape of the meniscus and therefore without altering the total free surface energy water-air. If h be the equilibrium height of the liquid, δh the increase to this and r the radius of the tube, the surface glass-air will be diminished and the surface glass-water increased by an amount $2\pi r\,\delta h$ cm.^{2} The surface energy will thus be diminished by $(\sigma_2 - \sigma_{1\cdot 2})\,2\pi r\,\delta h$. The potential energy due to gravity will be at the same time increased by $g\pi r^2 h\,(\rho_l - \rho_g)\,\delta h$ where ρ_l, ρ_g are the densities of water and air

respectively. Since the resultant energy change must be zero, we have

$$(\sigma_2 - \sigma_{1\cdot 2})\, 2\pi r\, \delta h = g\pi r^2 h\,(\rho_l - \rho_g)\,\delta h,$$

$$\therefore\ h = \frac{2(\sigma_2 - \sigma_{1\cdot 2})}{gr\,(\rho_l - \rho_g)}.$$

Now $\sigma_2 - \sigma_{1\cdot 2} = \sigma_1 \cos\alpha$ where α is the angle of contact,

$$\therefore\ h = \frac{2\sigma_1 \cos\alpha}{gr\,(\rho_l - \rho_g)}.$$

If the tube is not infinitesimal in radius, the calculation becomes more difficult, because we shall have to consider not only the form of the meniscus (in order to calculate its volume) but also the direction in which that form tends to change under the disturbance imagined. The general problem has been solved by Rayleigh (*Proc. Roy. Soc.* A, XCII. 184, 1915) for sufficiently small tubes with the result

$$\frac{2\sigma\cos\alpha}{g\,(\rho_l - \rho_g)} = r\,(h + r/3 - 0{\cdot}1288r^2/h + 0{\cdot}1312r^3/h^2).$$

For very large tubes Rayleigh finds

$$\frac{r\sqrt{2}}{a} - ln\,\frac{a}{h\sqrt{2}} = 0{\cdot}8381 + 0{\cdot}2798\,\frac{a}{r\sqrt{2}} + \frac{1}{2}\,ln\,\frac{r\sqrt{2}}{a}$$

where $a^2 = \dfrac{2\sigma\cos\alpha}{g\,(\rho_l - \rho_g)}$. This formula is accurate enough for any practical purpose if $\dfrac{r\sqrt{2}}{a} > 6$.

For intermediate values of r/a, or for tubes of intermediate size, no general formula has been given. Bashforth and Adams have however published tables from which the form of any capillary surface may be calculated, and with the aid of these Sugden has further calculated a table of values of r/b for all values of r/a between 0 and 6. b is here the radius of curvature at the crown of the meniscus, and since $h = \dfrac{2\sigma_1\cos\alpha}{g\,(\rho_l - \rho_g)\,b}$ accurately, the capillary

rise for a tube of any diameter may be calculated (Sugden, *J.C.S.* CXIX. 1483, 1921). This table is reproduced in part below:

$\frac{r}{a}$	$\frac{r}{b}$	$\frac{r}{a}$	$\frac{r}{b}$
0	1	0	1
0·1	·9968	0·9	·7875
0·2	·9869	1·0	·7490
0·3	·9710	1·5	·5545
0·4	·9498	2·0	·384
0·5	·9236	3	·149
0·6	·8936	4	·056
0·7	·8606	5	·020
0·8	·8249	6	·006

The capillary rise h, which has been discussed hitherto is of course the height of the capillary meniscus above that of an unbounded expanse of liquid, whose level is therefore unaffected by surface tension. In practice it is not usually convenient to employ so large a quantity of liquid as is demanded by this condition, but instead two interconnected tubes one of capillary, and one of wide bore are filled with liquid. The height h between the two liquid levels is now the difference between two quantities h_1 and h_2 defined by

$$h_1 = \frac{2\sigma \cos \alpha}{g(\rho_l - \rho_g) b_1},$$

and

$$h_2 = \frac{2\sigma \cos \alpha}{g(\rho_l - \rho_g) b_2},$$

whence

$$h = h_1 - h_2 = \frac{2\sigma \cos \alpha}{g(\rho_l - \rho_g)}\left(\frac{1}{b_1} - \frac{1}{b_2}\right).$$

To obtain reliable results it is essential in the first place to ensure purity of the liquid and absolute cleanliness of the apparatus especially from oily or greasy matter. The latter can most readily be removed by treating the apparatus, after preliminary cleansing, with warm aqua regia or chromic acid, and finally steaming for about half an hour. The apparatus should therefore be designed to facilitate this thorough cleaning. These conditions of course apply equally to any method of measuring surface tensions.

The diameter of the capillary tube must be known with accuracy and the cross-section must be truly circular. It is not as a rule easy to obtain tubing of uniform circular bore*, but in default of time for the tedious process of calibrating tubing the difficulty may be overcome by the following method due to Ferguson (*Proc. Phys. Soc.* XXXVI. 37, *1923*): Lengths of capillary tube are examined under a micrometer until one is found whose end cross-section is circular. This tube is then used so that the measured end dips downwards into the liquid; the upper end, instead of being open to the atmosphere is connected to a source of pressure and a manometer, and the meniscus is forced down until its lowest point is level with the end of the tube, so as to be observed at the only point where its curvature is accurately known. If then p be the pressure in dynes/cm.^{2} recorded by the manometer we have

$$2\sigma \cos\alpha\left(\frac{1}{b_1}-\frac{1}{b_2}\right)=gh(\rho_l-\rho_g)+p.$$

The first term may now be negative.

In Ramsay's experiments the forms of apparatus used were capable of sustaining pressures up to 100 atmospheres. The wide and narrow tubes were concentric: the wide tube was therefore annular in shape, and the allowance for the capillary rise in it becomes difficult to calculate. Ramsay did not make a sufficient allowance for the rise in the annular tube and in consequence all his values, and those of later workers who have adopted his figures for purposes of calibration for surface tensions are too low. Sugden has used an approximate method of correcting for the rise in the annulus, in which he considers a capillary tube of circular bore which gives an identical rise at a particular temperature and for a particular liquid, and assumes that the rise in the two tubes will be the same for all other temperatures and liquids. By this means he has, with the help of later measurements, corrected all Ramsay's values for which sufficient data are given in the original papers.

Very careful measurements by the method of capillary rise have been carried out by Volkmann, v. Szyszkowski, Richards and Harkins.

* Harkins tested several hundreds of feet of tubing before finding a length suitable for this purpose.

Modifications of the method.

Instead of a capillary dipping into a large vessel of liquid, we may reduce the quantity of fluid needed and simplify the measurement of the height h by using a U-tube of which one branch is of capillary and the other of wider bore. The difference h of height between the liquid in the two branches can then be easily read by means of a cathetometer or found by a slight modification of Ferguson's method.

Again the case of two parallel plates dipping vertically or inclined at a slight angle at a short distance apart in the liquid closely resembles that of the capillary tube and has been used by Quincke and Volkmann.

For the case of the parallel plates the equation for the surface tension is approximately

$$\sigma = \frac{dhg\,(\rho_e - \rho_g)}{2}$$

where d is the distance between the plates. This method compares unfavourably with the preceding ones, owing to greater difficulties of adjustment, the necessity for using optically plane glass, and larger quantities of liquid.

5. The drop weight method.

The method of measuring the surface tension of a liquid from the weight of a drop formed slowly and allowed to drop from a tip ground plane which is with a sharp circular edge, has frequently been employed owing to the simplicity of the method. The experimental difficulties to be overcome in order to obtain reproducible results consist in great measure of ensuring that the drop shall be allowed to form on the tip, which the liquid must wet uniformly, so slowly that it is practically in static equilibrium at the moment before it is detached. Loss by evaporation from the receiving vessel may thus be an important factor for which correction must be applied. Again for many solutions the rate at which the gas-liquid interface attains equilibrium is extremely slow, this is especially true for many solutions of biological importance which contain materials of low diffusivity. Thus it may be necessary to permit a drop to hang under conditions approaching its maximum size for several minutes to ensure the attainment of such equilibrium.

Tate (*Phil. Mag.* XXVII. 176, 1864) discovered empirically that the weight of a drop of liquid falling from the end of a tube was proportional to the radius of the tube and the surface tension of the liquid.

The theoretical formula for the maximum weight of a cylindrical drop hanging from a tube in equilibrium was shown to be

$$W = \pi r \sigma$$

by Worthington (*Proc. Roy. Soc.* XXXII. 362, 1881; *Phil. Mag.* 1884, 1885) and Rayleigh (*Phil. Mag.* XLVIII. 321, 1899).

Rayleigh showed however that in practice this equation required modification and found for tubes of moderate radius that a better agreement was obtained by the relationship

$$W = 3{\cdot}8 r \sigma.$$

For very small or very large tubes however the value of the "constant" 3·8 rises well above 4.

Morgan and his co-workers (*J.A.C.S.* 1908–1913) have published a number of papers in support of "Tate's laws" claiming that under suitable conditions $W = K r \sigma$ where K is a constant. This view however cannot be substantiated.

This variation is of course due to the fact that the actual detachment of the drop is an extremely complicated dynamical process (cf. Perrot, *J. Chim. Phys.* XV. 164, 1917).

Löhnstein (*Zeit. f. Physikal. Chem.* LXIV. 686, 1908) and Harkins (*J.A.C.S.* XXXVIII. 228, 1916, *et seq.*) assumed that the weight of an "ideal" drop should be given by the relationship

$$W = 2\pi r \sigma$$

and that for actual drops an empyric factor had to be introduced, the Löhnstein correction. This factor was dependent on the radius of the tip and the nature of the liquid under investigation. The Löhnstein equation in its final form is accordingly

$$W = 2\pi r \sigma f \frac{r}{a} \text{ where } a^2 = \frac{2\sigma}{\rho}.$$

The function was found to be approximately a cubic function of $\frac{r}{a}$ being unity when $\frac{r}{a}$ approaches 0 falling to a minimum of about 0·6 when $\frac{r}{a} = 1{\cdot}1$ and rising thereafter continuously.

In the light of the investigations of Rayleigh however it is evident that the basic assumption as to the weight of an "ideal" drop formed on the end of a tube of definite radius is erroneous.

A return to a more rational expression of the relation between drop weight and surface tension has been made by Iredale (*Phil. Mag.* XLV. 1088, 1923). This expression rests upon the fact that different liquids may form drops of similar shape from tubes of different diameters. From this and from the assumption that rupture occurs at the point of maximum concavity the equation

$$K^2 = \frac{\sigma_1 \rho_2}{\sigma_2 \rho_1}$$

is developed, where σ_1, σ_2 and ρ_1, ρ_2 are the surface tensions and densities respectively of two liquids and K is the ratio of the radii of the tubes from which symmetrical drops hang. All that is required for the practical determination of surface tension from this formula "is a knowledge of the tube radius and drop radius ratio, with a continuously varying radius of tube, for some standard liquid of known surface tension and density" (Iredale, *loc cit.*).

From the data of Harkins on the drop weights of water from tubes of varying radius we obtain the following data for the radius of drops of water formed at tips of various sizes:

Tube radius r in cms.	Drop radius r' for water	$\frac{r}{r'}$
·09946	·1998	·4977
·14769	·2238	·6603
·19666	·2425	·8112
·23790	·2555	·9863
·27605	·2669	1·035
·29694	·2727	1·088
·32362	·2797	1·157
·37964	·2938	1·289
·44755	·3103	1·442
·55009	·3351	1·643
·65031	·3581	1·816
·72229	·3744	1·929
·77329	·3829	2·019
·84892	·3888	2·184
1·0028	·3900	2·571

With the aid of this table and the equation of symmetry we are in a position to calculate the surface tensions of other liquids from

a knowledge of the drop weight and the tip radius alone. The following example given by Iredale may be cited.

The weight of a mercury drop detached from a capillary tube of radius 0·0852 cm. was found to be 0·1794 gm. Since $\rho = 13{\cdot}53$ for mercury the radius of the mercury drop is 0·1469 cm. Hence

$$\frac{r}{r'} = \frac{0{\cdot}0852}{0{\cdot}1469} = 0{\cdot}5801.$$

From a graph constructed from the table above we find that the tube radius required to give a drop of water of the same characteristic ratio $\frac{r}{r'}$ would be 0·1239 cm. Hence

$$K = \frac{0{\cdot}0852}{0{\cdot}1239},$$

also $\sigma_{H_2O} = 72{\cdot}80$ and $\rho_{H_2O} = 0{\cdot}998$ whence

$$\sigma_{Hg} = \frac{K^2 \rho_{Hg} \sigma_{H_2O}}{\rho_{H_2O}} = 466 \text{ dynes per cm.}$$

Many modifications of the drop weight method have been utilised in practice.

Instead of measuring the weight directly we may calculate it from the volume and the density: the drop volume method has been applied by Harkins chiefly to the measurement of the tension between two liquid phases, and it probably falls little short in accuracy from the previous method. More frequently it has been modified, especially for biochemical purposes, as a drop number method: that is, a known volume of liquid is allowed to flow out of a tube, and the number of drops formed is compared with that formed by a standard fluid. This method is necessarily very rough.

Bubble pressure.

By reversing the position of liquid and gas assumed in the preceding section we obtain the bubble pressure method. The theory corresponds closely with that of the drop weight and has been developed by Cantor, Feustel and Schrödinger (*Ann. d. Physik*, XLVI. 413, 1915).

The equation derived is

$$\sigma = \frac{1}{2} rp \left(1 - \frac{2}{3}\frac{r\rho}{p} - \frac{1}{6}\frac{r^2\rho^2}{p^2}\right)$$

where p is the maximum pressure, and r is now the internal radius of the tube.

The experimental method has been most carefully worked out by Jäger (*Koninkl. Akad. Amsterdam,* XVII. 521, 1914), in researches extending over a very wide temperature range. The liquid under investigation is contained in a long narrow bulb through which a tube of glass or platinum is sealed at the top and dips into the liquid, while a second tube is sealed on at right angles near the top. The upper tube is connected to a reservoir of pure nitrogen and to one arm of a manometer whose other arm is in connection with the tube. This method of course gives the surface tension of the liquid against nitrogen saturated with its vapour: and probably differs little as we shall see (pp. 57–58) from that against the pure vapour.

This method undoubtedly has the widest application of any yet employed, and is at the same time accurate. Among other workers who have used it are Cantor (*Wied. Ann.* XLVII. 399, 1892), Forch (*Ann. Phys. u. Chem.* LXVIII. 801, 1899), Jäger (*Zeit. f. anorg. u. allgem. Chemie* CI. 1, 1917), Lineharger (*J.A.C.S.* XXII. 5, 1900), and Whatmough (*Zeit. Physikal. Chem.* XXXIX. 129, 1902).

6. Dynamic methods.

Two dynamic methods have been developed for measurement of the surface tensions, the method of ripples first employed by Rayleigb and the vibrating jet method developed by Bohr.

In the ripple method a series of ripples is caused to travel over the surface of the liquid, the ripples being formed by means of an oscillating glass plate attached to an electrically driven tuning fork dipping into the liquid. If viewed by means of intermittent illumination conveniently arranged by periodic interception of the light by interposition of a screen attached to one limb of the fork, apparently stationary waves may be observed and the mean wave length readily determined.

The velocity of propagation of the ripple depends on the surface tension of the liquid. Rayleigh (*Phil. Mag.* XXX. 386) showed that the velocity of a ripple moving over a horizontal layer of liquid of surface tension σ was expressed by means of the equation

$$v^2 = \frac{\lambda g}{2\pi} + \frac{2\pi\sigma}{\lambda\rho}$$

where λ is the wave length of the ripple.

If the time of vibration of the tuning fork be τ, then

$$\tau = \frac{\lambda}{v},$$

whence $$\sigma = \rho\left\{\frac{\lambda^3}{2\pi\tau^2} - \frac{g\lambda^2}{4\pi^2}\right\}.$$

The method has been employed by Dorsey (*Phys. Rev.* v. 213, 1897) and Grünmach (*Ann. der Physik*, XXXVIII. 1018, 1912) for the determination of the surface tensions of a number of salt solutions. It will be noted that σ is dependent on the cube of the wave length, a factor militating against the general adoption of this method for the accurate determination of the surface tension. Again it is a difficult matter to decide how far such a method really yields a true value for the dynamic surface tension.

As we shall have occasion to note in dealing with solutions, the composition of the surface phase is very different from that of the bulk liquid. When a liquid interface is newly formed the system is unstable until the surface phase has acquired its correct excess or deficit of solute by diffusion from or into the bulk of the solution. This process of diffusion is by no means instantaneous and, as has been observed in discussing the drop weight method, several minutes may elapse before equilibrium is established. In the ripple method the surface is not renewed instantaneously but may be regarded as undergoing a series of expansions and contractions, thus we should anticipate that the value of the surface tension of a solution determined by this method would lie between those determined by the static and an ideal dynamic method respectively.

More closely approaching the conditions desirable for determining the true dynamic surface tension is the vibrating jet method.

If a stream of liquid be forced through a small jet of elliptical cross section it will be observed that the issuing jet is in apparent vibration and forms a series of nodes equidistant from one another. From a determination of the wave length of the vibration, a measurement which can be made with some accuracy provided that the stream of liquid issues at a constant speed, the surface tension of the liquid may be determined by means of the following equation developed by Bohr.

If v be the velocity of outflow, $r_{max.}$, $r_{min.}$ the semi-major and minor axes of the jet, a the mean radius, $\frac{b}{a}$ the amplitude $= \frac{r_{max.} - r_{min.}}{r_{max.} + r_{min.}}$, ρ the density of the liquid and σ its surface tension, ρ_1 the density of the gas above the liquid, λ the wave-length, η the viscosity of the liquid, Bohr showed that

$$\sigma = \frac{4\pi^2}{\lambda^2} v^2 a^3 (\rho + \rho_1) \frac{\left[1 + \frac{37}{24}\left(\frac{b}{a}\right)^2\right]}{\left[6 + 10\left(\frac{\pi a}{\lambda}\right)^2 + 2\cdot5\left(\frac{\pi a}{\lambda}\right)^4\right]} \cdot \left[1 + \frac{\eta\lambda}{\rho v a^2 \pi} + \ldots\right]^{\frac{3}{2}}.$$

The term $\left[1 + \frac{\eta\lambda}{\rho v a^2 \pi} + \ldots\right]^{\frac{3}{2}}$ however even in 23 °/₀ cane sugar solution is only 1·0002 and can therefore be considered as unity.

This method has been employed by Schmidt (*Zeit. Physikal. Chem.* XXXIX. 1108, 1912) for determining the surface tension of amalgams and by Stocker (*Zeit. Physikal. Chem.* XCIV. 149, 1920) for solutions with satisfactory results.

Static and Dynamic Surface Tension.

The static methods of measuring surface tension lead to values of this quantity for a surface which has been in existence for a considerable period of time, varying from a minute or less, when the drop-weight metbod is used upwards. The different static methods appear as a rule to lead to similar results for the surface or interfacial tension of the same liquid. Dynamic methods measure the tension of a surface which must necessarily have existed for a much shorter period of time before the determination: for example, in the vibrating jet method the age of the surface may be as little as 0·01 second, while by a modification of the capillary rise method due to Lenard and Hiss, the tension may be investigated of a surface whose age is not more than 0·001 second. The dynamic methods give rise to results which differ more among themselves and from those of static methods, and it is natural to assume in explanation of this difference that the equilibrium conditions at the surface have not in all cases been obtained. Further work on the dynamic surface tensions of associated liquids and of solutions containing solutes of varying diffusivity

should throw light on the important question of the rate of attainment of equilibrium in the surface phase.

7. The total surface energy.

The relationship between surface tension and temperature leads to a series of interesting results bearing upon chemical constitution and the structure of the surface layer. As we have seen the surface tension is numerically equal to the free surface energy from which with the aid of the temperature coefficient the total surface energy may be obtained.

In the following table a few values of the free surface energies and the temperature coefficients are given.

Liquid	σ_0	$-\frac{d\sigma}{dT}$
Water	75·87	0·1511
Carbon disulphide ...	37·71	0·1607
Mercury	480·30	0·2330
Hexane	21·31	0·1039
Octane	23·36	0·0920
Chloroform	28·77	0·1134
Phenol	42·27	0·1050

Since $\frac{d\sigma}{dT}$ is always negative for pure liquids the total surface energy is greater than the free energy; moreover, as the surface tension decreases roughly in a linear manner with elevation of the temperature, the total surface energy remains approximately constant over a considerable temperature range and is a convenient quantity to use in the comparison of the surface behaviour of different liquids.

As examples of the magnitude of variation in the free surface energies and the approximate constancy of the total surface energies the following data for benzene (Whittaker, *Proc. Roy. Soc.* A, LXXXI. 21, 1900), mercury and carbon tetrachloride (Harkins and Roberts, *J.A.C.S.* XLIV. 656, 1922) may be cited (see tables, p. 20).

A critical examination of the total surface energies of various liquids has been made by Langmuir and Harkins. It is found that the surface energies of the aliphatic hydrocarbons are mainly independent of the length of the hydrocarbon chain, whilst the surface

energies of the alcohols are but slightly larger than those of the corresponding hydrocarbons. Langmuir in his investigations on the behaviour of thin films of insoluble fatty acids and alcohols on the surface of water (Ch. III) came to the conclusion that such molecules were orientated in the surface with their hydrocarbon chains in the gas phase and their polar carboxyl or hydroxyl groups in the water phase. If we assume a similar orientation of the surface film of a homogeneous liquid and that the surface energy is defined by the nature of the surface film alone the experimental facts may be interpreted at least in a qualitative way. For hydrocarbons will expose the methyl groups at the ends of the chains to the air whilst fatty acids and alcohols will likewise possess a surface layer of CH_3 groups, the polar —COOH and —OH being immersed in the bulk of the liquid. We thus arrive at a hypothesis as to the structure of the surface phase for pure liquids, that it consists of a layer of orientated molecules with the active portions of the molecule drawn inwards and that the total surface energy is determined by the nature of the external groups of the molecules. It is probable however that this assumption whilst expressing the limiting ideal conditions of such a surface film does not represent the properties of actual films.

Benzene			
Temp. °K.	σ ergs per sq. cm.	$\frac{d\sigma}{dT}$	U ergs per sq. cm.
353	20·28	−0·111	59·5
363	19·16	−0·113	60·2
373	18·02	−0·115	60·9
383	16·85	−0·1155	61·1
393	15·71	−0·1145	60·7
413	13·45	−0·111	59·4
433	11·29	−0·108	58·0
453	9·15	−0·104	56·1
473	7·17	−0·099	54·0
493	5·25	−0·094	51·5
513	3·41	−0·087	48·1

Mercury			
Temp. °K.	σ ergs per sq. cm.	$\frac{d\sigma}{dT}$	U ergs per sq. cm.
313	479·7	−·233	552·6
363	468·0	−·233	552·6
413	456·4	−·233	552·6
443	449·4	−·233	552·6
Carbon tetrachloride			
313	24·41	−·117	60·87
413	12·22	−·103	54·80
463	7·28	−·095	51·26
503	3·56	−·087	47·30
523	1·93	−·076	41·68
533	1·20	−·067	36·91

In the case of water for example we must assume on this hypothesis a layer of orientated molecules on the surface of the liquid. The surface molecules however are continually evaporating and recondensing on the surface. The rate of evaporation and condensation may readily be determined with the aid of the Herz-Knudsen *effusion equation* (see p. 138)

$$\mu = \frac{KP}{\sqrt{MT}},$$

where μ is the rate of effusion, P the vapour pressure and M the molecular weight. At 20° C. the rate of evaporation is some 10^{22} molecules per sq. cm. per second or the life of a molecule on the surface is only 10^{-7} seconds. During this small period of time the molecule must become orientated and assume a vertical posture about which mean position it must oscillate. This order of time although small does not necessarily necessitate a rejection of the hypothesis for the moment of inertia of a water molecule is extremely small*.

The other assumption that the total surface energy is determined by the nature of the external groups of the molecules is capable of more direct proof. We find for example that the total surface energy increases in aliphatic compounds as H is replaced in the order: OH, NH_2, CN, I, SH, COOH, NO_2, $COOCH_3$, COCl, $CONH_2$. Evidently the assumption is not strictly true, for these substituent groups should not affect the surface tension of a hydrocarbon, CH_3, surface. Langmuir assumes that these larger groups force apart the surface molecules and that the forcing apart of these groups increases the surface energy.

Langmuir and Harkins from an examination of the total surface energy of benzene and substituted derivatives came to the conclusion that this molecule lay as a flat ring on the surface, but by the introduction of a polar group the ring was tilted on edge causing a rise in the surface energy, according to Harkins by permitting the residual valencies of the carbon atoms in the ring to come into play. An alternative suggestion is that owing to the tilt more molecules can be accommodated on the surface. Harkins further

* The natural period of a molecule as determined from both the thermal conductivity and from the natural infra-red vibration frequency is of the order of 10^{-13} seconds.

attempts to explain the differences of behaviour between the ortho- and para-compounds in various cases by similar assumptions, which do not seem to be in close accord with the experiments. (See also King and Wimpler, *J.A.C.S.* XLIV. 1894, 1922.)

Sugden (*J.C.S.* CXXV. 1167, 1924) has examined the total surface energies of a number of para-substituted benzene compounds. If these compounds are orientated so that the surface molecules are perpendicular to the surface, the area occupied by each molecule is simply that of the cross section of the benzene ring. This avoids the complication that different molecules might occupy different areas. If we take a series of para-compounds $X\phi Y_1, X\phi Y_2, \ldots X\phi Y_6$, the groups Y_1—Y_6 having progressive residual affinities, the residual affinity of the group X lying between Y_3 and Y_4, the molecules should orientate themselves in the following manner:

Y_1	Y_2	Y_3	X	X	X	Vapour
X	X	X	Y_4	Y_5	Y_6	Liquid

and the surface energies of the first three compounds should progressively increase whilst those of compounds 4, 5, 6 should be identical.

Further if we take a series $Y_2\phi Y_1$, $Y_2\phi Y_3$, $Y_2\phi Y_4$ none of these compounds should have a surface energy greater than that of $Y_2\phi Y_3$ or $X\phi Y_2$, since Y_2 is the greatest residual affinity which is lifted into the surface. The following values are taken from Sugden's paper:

Y	CH_3	H	Cl	Br	I	NO_2	NH_2
X = H	65·53	70·26	71·01	74·48	77·07	81·70	82·40
= Cl	66·65	71·01	71·45	71·83	74·71	78·68	81·37
= CH_3	—	65·53	66·65	66·46	69·28	74·06	68·19

On the strict theory of orientation the data in the first horizontal series must be interpreted on the assumption that the substituent groups are all in the vapour phase the hydrogen being in the liquid, a conclusion quite opposite to that usually obtained. In the second

and third series according to the above reasoning the surface energy of chlorbenzene and toluene should have been the respective maxima.

We must conclude that the surface tension of a pure liquid is determined by properties of the molecule as a whole together with its foundation rather than by the external groups only.

In the case of solutions also Goard has noted that in phenol solutions possessing identical surface concentrations of phenol the surface tension varies with the nature of the underlying bulk phase, being higher for solutions containing salt (see p. 42).

8. The surface energy and latent heat of evaporation.

Many attempts have been made to correlate the latent heat of evaporation of a liquid and its surface tension (see Edser, *Fourth Report on Colloid Chemistry*). The process of evaporation may be considered to take place in two stages. In the first it is brought from the interior to the surface overcoming the surface tension, in the second it vaporises from the surface film. According to Laplace's theory of a diffuse gradient of properties between bulk liquid and vapour we should anticipate that the molar surface energy should be half the molar internal latent heat, a generalisation known as Stefan's law (*Wied. Ann.* XXIX. 655, 1896). On the conception however of a discrete surface of separation it is evident that this should not be the case, for a molecule proceeding from the interior to the surface requires the supply of sufficient energy to remove the non-polar end of the molecule from the liquid to the vapour phase, it being still attached by the polar end to the bulk liquid phase. The second process of superficial vaporisation entails the separation of the active group from the liquid.

Clearly equality between the two stages in the process of evaporation from the interior of the liquid should only obtain for perfectly symmetrical molecules; with increasing asymmetry, the second step or the detachment of the polar end of the molecule should become more important and the energy associated with this rupture will be a larger fraction of the total energy of vaporisation. An examination of the surface energy and latent heats of evaporation for a series of compounds at corresponding

temperatures has been made by Harkins and Roberts (*J.A.C.S.* XLIV. 653, 1922), some of whose results are given in the following table:

Liquid	Corresponding temperature 0·7 of T_c. ϵ total surface energy per molecule $\times 10^{14}$ ergs	λ internal latent heat of vaporisation per molecule $\times 10^{14}$ ergs	$j=\lambda-\epsilon$ energy changed from potential to kinetic when molecule jumps from surface to vapour, per molecule $\times 10^{14}$ ergs	$\frac{\epsilon}{\lambda}$
Nitrogen	3·84	8·7	4·8	0·514
Carbon tetrachloride	18·2	40·2	22·0	0·452
Benzene	18·4	41·7	23·3	0·441
Chlorbenzene ...	20·3	48·8	28·5	0·417
Ethyl alcohol ...	11·2	59·3	48·1	0·186
Methyl alcohol ...	8·5	51·6	43·1	0·164

It will be noted that the symmetrical compound carbon tetrachloride differs markedly in the ratio $\frac{\epsilon}{\lambda}$ from the unsymmetrical methyl alcohol.

9. The influence of temperature on the surface tension of liquids.

The surface tension of all liquids decreases as the temperature rises. Over small ranges of temperature the relationship is with few exceptions linear

$$\frac{d\sigma}{dt} = -K$$

or

$$\sigma_t = \sigma_0 (1 - at),$$

where

$$K = a\sigma_0.$$

At the critical temperature the distinction between the two phases and consequently the surface tension disappears. The absolute magnitude of the surface tension therefore depends to a great extent upon the distance from the temperature of observation to the critical point, thus we find that while the permanent gases have tensions never exceeding a few dynes per cm., in the case of liquefied metals the surface tensions may exceed a thousand.

Ramsay and Shields and Walden concluded from their experiments that a linear relation held almost up to the critical point and write

$$\sigma = c\,(T_c - T - \delta),$$

where T_c and T are the critical and observation temperatures, c and δ constants. Van der Waals in his theory of capillarity developed the equation

$$\sigma = \sigma_0 \left(1 - \frac{T}{T_c}\right)^{\frac{3}{2}}.$$

Hence

$$\frac{1}{\sigma_0}\frac{d\sigma}{dT} = \frac{3}{2}\sqrt{1 - \frac{T}{T_c}} \times \left(-\frac{1}{T_c}\right)$$

and $\frac{d\sigma}{dT}$ vanishes with σ at the critical point. Experiment however agrees better with a modified formula

$$\sigma = \sigma_0\left(1 - \frac{T}{T_c}\right)^n,$$

where n varies somewhat for different liquids but is in the neighbourhood of 1·21 as determined by Ferguson (*Trans. Farad. Soc.* XIX. 408, 1923).

10. Eötvös' Law.

The variation of surface tension with the temperature has been studied by many observers with the view of testing the theory of Eötvös that the molar free surface energy of any liquid should be proportional to the distance from its critical temperature and to a universal constant, a "law" analogous to the gas law $PV = RT$, the product PV being the free molar volume energy of the gas. Correspondingly in the case of the liquid-vapour surface the molar free energy is proportional to the product of σ and the surface occupied by a gram molecule or to $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$, where M is the molecular weight and ρ the density of the liquid. (On the assumption that the molecules are symmetrical in shape.)

Instead of T we write $T_c - T$ and obtain

$$\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K(T_c - T),$$

where K is a universal constant of approximate value 2·2.

Ramsay and Shields tested this relation for a large number of liquids and modified it to $\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}} = K(T_c - T - \delta)$, since the molar surface energy appeared to vanish at a temperature somewhat below the critical point.

To avoid the necessity for determining the critical temperature we may differentiate and write

$$K = \frac{d}{dT}\left\{\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}\right\},$$

or assuming that M is independent of the temperature (i.e. for non-associated liquids)

$$K = M^{\frac{2}{3}}\frac{d}{dT}(\sigma\rho^{-\frac{2}{3}}).$$

Katayama (*Tokio Univ. Sci. Rep.* IV. 5. 373, 1916) examined an equation of the type

$$\sigma\frac{M^{\frac{2}{3}}}{(\rho_l - \rho_v)^{\frac{2}{3}}} = K(T_c - T),$$

and showed that this represented the results of experiment over the full range of temperature from freezing to critical point which Ramsay's equation even when modified fails to do.

An examination of the data however indicates that the constant

Less than 2·2		Greater than 2·2	
Liquid	K	Liquid	K
Ethyl alcohol ...	1·08	Methylbenzoate	2·32
Acetonitrile ...	1·44	Paraldehyde	2·37
Propyl alcohol ...	1·40	Phenetole	2·56
Amyl alcohol ...	1·35	Phenylisosulphocyanate	2·32
n-Butyric acid ...	1·57	Diethylaniline	2·337
Iso-butyric acid	1·66	Diphenylamine	2·57
Acetic acid ...	0·95	Dimethyl-o-toluidine ...	2·49
Glycol	1·03	Benzophenone	2·63
Caproic acid ...	1·62	Anisole	2·358
Phenol	1·70	Quinoline	2·43
p-Tolunitrile ...	1·72	Ethyl esters of	
		Propionylmalic acid ...	2·87
		Butyrylmalic „ ...	3·18
		Valerylmalic „ ...	3·40
		Caproylmalic „ ...	3·04
		Pelargonylmalic „ ...	3·68
		Capronylmalic „ ...	3·59

K of Eötvös' equation is by no means a universal constant of mean value 2·2, as is revealed by the table on p. 26.

For a considerable group the temperature coefficient of the molecular surface energy $\frac{d}{dT}\left\{\sigma\left(\frac{M}{\rho}\right)^{\frac{2}{3}}\right\}$ is found to be in the neighbourhood of 2·2: this group included the saturated hydrocarbons, liquids which of all others would be expected to exist as simple unassociated molecules. (For argon, nitrogen, and carbon monoxide, Baly and Donnan found values of K very close to 2·0.)

In a second group which includes water, the lower fatty acids and alcohols, amines, nitriles and phenols, values of K considerably below 2·2 are found. Since other grounds, such as abnormal coefficients of expansion and specific inductive capacity, indicate that these substances are probably associated to some extent, Ramsay and Shields attempted to bring the coefficients of molecular surface energy into line with those of the first group by replacing M, the formula weight, by αM, where α is the degree of association and αM therefore the mean molecular weight. In this procedure it is assumed that the average composition of the surface layer is the same as that of the liquid in bulk, for otherwise the value of α obtained can apply only to the surface layer. In order to decide this question, Ramsay and Aston examined the surface tensions at different temperatures of mixtures of organic liquids of different molecular weights and compared the values of K for the mixture in each case with that calculated from the K of the components and their molecular proportions in the mixture. The calculated and observed values of K agreed within the limits of experimental error and it was concluded that the assumption made was justified. Unfortunately, however, the examples chosen are not sufficient to prove the case, for in no example do the surface tensions of the liquids differ by more than six dynes per centimetre, so that little deviation from a simple mixture rule could be expected. If instead of two organic liquids with not very different surface tensions the experiment had been carried out with water and an alcohol, a different conclusion would have been reached. Undoubtedly the mean molecular weights in the surface and the liquid differ greatly in such a case. Now where we are dealing with a simple liquid

and its polymeric modification we should expect to find that the order of difference between their surface tensions in an imaginary pure state would be large; in order to illustrate this point the example of Walker (*Phil. Mag.* XLVII. 111, 1924) will be followed by constructing a table of surface tensions of pairs of compounds, one in each pair having approximately twice as large a nucleus as the other.

Temp.	Liquid 1	σ_1	Liquid 2	σ_2
129·2	Benzene	14·71	Diphenyl	28·64
108·3	Toluene	19·6	Dibenzyl	27·86
−39·1	Propane	14·95	Hexane (extrapolated)	22·76
20	*i*-Pentane	13·72	Di-isoamyl	22·24
20	Methylene chloride	26·52	Acetylene tetrachloride	34·1
24·9	Ethyl formate ...	22·9	Ethyl oxalate	31·4
0	Amyl acetate ...	26·6	Amyl succinate ...	30·9

In an extreme case the surface tension of diphenyl is almost double that of benzene at the same temperature and it would be expected that in a mixture of these substances the benzene would be preferentially adsorbed at the surface, and any attempt to find the mean molecular weight of the two would break down. Certain mixtures of aniline and water were found by Worley (*J.C.S.* CV. 260, 1914) to have positive temperature coefficients of surface tension as exemplified in the following data for a 3·3 °/ₒ aniline

Temp. ...	15° C.	55° C.	95° C.
σ ...	48·21	49·22	50·73 dynes per cm.

solution; this would lead to a mean molecular weight less than zero. Such criticisms suggest that although a deviation below the normal value of K does indeed indicate that there is association the degree to which it occurs cannot be obtained as simply as was assumed.

Another amendment to the simple rule of Eötvös is made necessary owing to the existence of a third class of bodies with exceptionally high values of K. Such for example are the higher fatty acids and their glycerides, investigated by Walden. We cannot assume dissociation in the pure liquid state, for even when dissolved in dissociating media there is no physical evidence of it.

The simplest explanation in harmony with the theory of Eötvös is furnished by the observation that bodies of this third class possess in all cases long chains of atoms so that the molecule must present a highly unsymmetrical appearance. The molecular surface will, if the molecules lie flat in the superficial layer, considerably exceed the calculated amount $\left(\frac{M}{\rho}\right)^{\frac{2}{3}}$, and if they are orientated normally to the surface, fall much below this value. In the first case the calculated K would be lower and in the second higher than the normal value. This explanation is in harmony with other observed facts concerning long chain compounds, such as their tendency to form "liquid crystals," their orientation towards a water-air surface and the formation of micelles. When interpreting the observed values of K attention must be paid to the shape of the molecule and its orientation as well as to its state of association*.

Allusion has already been made to the Eötvös constants of liquids at low temperatures which are rather less in the cases quoted than the normal value for ordinary temperatures although there is very little probability of association, more especially in the case of argon. At still lower temperatures K. Onnes has found K for hydrogen to be 1·4, so that this coefficient diminishes as the absolute zero is approached. For helium we may expect that a very abnormally low K will be found.

It would be of much interest to have data for liquids whose molecules may with certainty be assumed spherical in form and not at all associated, for example of methane, tetramethylmethane or tricyclobutane. We should expect these liquids to have equal values of K unaffected by temperature, and the common value

* Conversely, from a knowledge of the value of K for an unassociated substance, conclusions may fairly be drawn as to the shape and orientation of its molecule, subject of course to limitations imposed by thermal agitation in the surface. For example, the value of K for the glycerides of oleic and palmitic acids reaches 6, or three times the normal value. If orientation is completely normal to the surface, this would correspond with a length some five times the diameter—much about what we should expect of these bodies if the three hydrocarbon chains lay parallel. The free acids have a much smaller K and since the ratio of length to diameter in their case must be even greater than for the glycerides we must conclude that there is far less orientation, but that the shape of the molecule allows more molecules to come into a given space of surface in a random disposition than would be the case for a molecule of the same volume but of regular shape.

would provide a starting point, the deviation from which gives a measure of the association or ellipticity of the molecules of other substances.

The Parachor.

Sugden (*J.C.S.* CXXV. 1177, 1924; CXXVII. 1525, 1868, 1925) has compared the molecular volumes of substances under conditions such that they possess identical surface tensions and has shown that they are determined by the molecular constitutions of the substances. In obtaining the 'parachor' P Sugden makes use of the approximate relationship between free surface energy and density noted by Macleod (*Trans. Farad. Soc.* XIX. 38, 1923)

$$\sigma = c\,(\rho_l - \rho_v)^4$$

where c is a characteristic constant independent of the temperature. The parachor P is $\sqrt[4]{c}\,.\,M$ or

$$P = \frac{\sigma^{\frac{1}{4}}}{(\rho_l - \rho_v)}\,.\,M.$$

P is found to be a function of the chemical constitution and to possess the following values:

C = 4·8,	treble bond = 46·6,
H = 17·1,	double bond = 23·2,
O = 20·0,	six ring = 6·1,
Cl = 54·3,	ester O = 60·0.
Br = 68·0,	
I = 91·0,	

CHAPTER II

THE SURFACE TENSION OF SOLUTIONS

1. The Gibbs Equation.

In the case of pure liquids the surface phase is naturally of the same composition as the bulk phase; for solutions on the other hand the composition of the surface phase need not necessarily be identical with that of the underlying solution. In general the addition of a solute to a solvent will affect the surface tension of the latter and since the energy of the system strives towards a minimum there will be a tendency if the solute lowers the surface tension of the solvent for the former to accumulate at the surface. If the solute elevates the surface tension of the solvent the reverse action occurs and the surface phase will be poorer in solute than the bulk phase. This enrichment or impoverishment of the surface phase does not continue indefinitely, for a point is reached when the action is balanced by the return from the enriched to the impoverished phase due to diffusion, the rate of which is proportional to the difference in osmotic pressures of the solute in the two phases.

The exact mathematical treatment for the calculation of the excess or deficiency of solute in the superficial phase was first made by Gibbs and independently a year later by J. J. Thomson, and Gibbs' equation may be regarded as the fundamental basis for the thermodynamical treatment of interfacial phases.

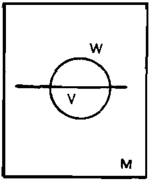
Gibbs' equation, which is perfectly general, may be deduced readily from the potential functions of Gibbs (*Thermodynamics*, p. 221) and Duhem (*Le Potential Thermodynamique*, Paris 1886), or in the following manner.

M is a vessel which encloses a system in equilibrium. W is a closed surface within the vessel which contains a volume V.

For any infinitesimal change in a reversible system, the change in energy may be written

$$dU = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \dots \quad \text{.........(1)},$$

where S is the entropy, μ_1, μ_2 the chemical potentials of the components. This equation is true whether the matter within the surface W is homogeneous or not, so long as W does not intersect a phase boundary. When this condition is not fulfilled, a term of the form σdA must be added to the right-hand side of equation (1) for each interface intersected and also the second term will have to be resolved into parts if any of these interfaces are appreciably curved.



Let us consider the case in which there are two phases separated by an interface of which only an area A is within the surface W and in which the interface is flat. We obtain

$$dU = TdS - pdV + \sigma dA + \mu_1 dm_1 + \mu_2 dm_2 + \dots \quad \dots\dots(2).$$

The non-homogeneous layer separating the phases is at least one molecule thick and may be thicker. Owing to lack of knowledge in this respect it is convenient to imagine a geometrical surface drawn somewhere in this non-homogeneous region and parallel to it. This surface will divide the volume V into two parts V' and V'' which we may assign to each of the phases.

By assuming that the entropies S', S'' in ergs per c.c. per ° C. and the densities of each component ρ_1', ρ_2', ρ_1'', ρ_2'', etc. in mols. per c.c. which obtain in the bulk of the two phases remain constant right up to the dividing surface, we can assign a portion of dU to each of the phases

$$dU' = Td(V'S') - pdV' + \mu_1 d(V'\rho_1') + \mu_2 d(V'\rho_2') + \text{etc.},$$

$$dU'' = Td(V''S'') - pdV'' + \mu_1 d(V''\rho_1'') + \mu_2 d(V''\rho_2'') + \text{etc.},$$

p having the same value in both phases if the interface dividing them is flat. To the sum of dU' and dU'' must however be added a third term dU_i relating to the interface. Thus

$$dU = dU' + dU'' + dU_i.$$

In a similar way an increment of entropy and quantities of components must be present in the interface

$$dS = d(V'S') + d(V''S'') + d(AS_i),$$

$$dm_1 = d(V'\rho_1') + d(V''\rho_1'') + d(A\Gamma_1),$$

where Γ_1 is the surface concentration of one component.

Whence it follows that

$$dU_i = Td(AS_i) + \sigma dA + \mu_1 d(A\Gamma_1) + \mu_2 d(A\Gamma_2) + \dots \quad \dots(3).$$

Let us now consider the energy required to increase the surface from an area A_0 to an area A.

The mechanical work required is $\sigma(A - A_0)$.

The heat required is $T(A - A_0)S_i$.

The chemical energy required is $\mu_1(A - A_0)\Gamma_1 + \mu_2(A - A_0)\Gamma_2$.

This last term is necessary since the amounts of the various components required to make up the surface concentration of the newly formed surface cannot be taken from the bulk phases inside the surface W without altering the μ values of the components. They must therefore be introduced from outside the system and the intrinsic energy associated with them must be added to the system. We thus obtain

$$U_i - U_{i_0} = \sigma(A - A_0) + T(A - A_0)S_i + \mu_1(A - A_0)\Gamma_1 + \mu_2(A - A_0)\Gamma_2 + \dots.$$

On differentiation we obtain

$$dU_i = \sigma dA + Ad\sigma + Td(AS_i) + AS_i dT + \mu_1 dA\Gamma_1 + A\Gamma_1 d\mu_1 + \mu_2 dA\Gamma_2 + A\Gamma_2 d\mu_2 + \dots \quad \dots(4).$$

Subtracting from (3) and dividing through by A we obtain

$$d\sigma = -S_i dT - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \dots.$$

For a binary system at constant temperature this reduces to

$$d\sigma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2.$$

If our geometrical surface, which we have placed arbitrarily in the non-homogeneous region, be drawn in such a position that Γ_1 is zero we obtain

$$d\sigma = -\Gamma_2 d\mu_2.$$

For ideal solutions the relationship between the chemical potential and the concentration is given by the expression

$$\mu = \mu_0 + RT \log_e c,$$

whence $\quad -d\sigma = RT \,.\, \Gamma \,.\, d\log_e c \quad$ or $\quad \Gamma = -\dfrac{d\sigma}{RTd\log_e c}.$

For all non-ideal and concentrated solutions the concentration may

be replaced by the thermodynamic concentration or "activity" fc defined by

$$\mu = \mu_0 + RT \log_e fc,$$

whence $$\Gamma = -\frac{d\sigma}{RTd \log_e fc}.$$

The Gibbs equation may be expressed in other forms such as

$$\Gamma = -\frac{d\sigma}{RTd \log_e P}$$

where P is the vapour pressure of the solute, or

$$\log_e fc = -\frac{1}{RT}\int \frac{d\sigma}{\Gamma}.$$

It is evident that the unit of concentration is immaterial, but that if R be given the value $1{\cdot}98J = 4{\cdot}316 \times 10^7$ ergs/degree, Γ will be expressed in grm. mols per sq. cm.

The quantity of solute Γ transferred from the interior to the surface may be called the adsorption per unit surface. It may be positive or negative according to whether the solute lowers or raises the surface tension of the solution. Gibbs' equation shows us that whenever we have two components present in a liquid whose surface tension would be increased by an increase in the concentration of one of them, that constituent must have a lower concentration relative to the other in the surface than in the homogeneous phase. The field covered by the theorem is very wide, for it applies not only to all solutions commonly so called, but to associated or dissociated liquids and to substances capable of undergoing isomeric or tautomeric or allotropic change in the liquid state. Every such binary liquid is bounded by a surface film characterised not only by possessing a certain energy but also by its composition.

2. The experimental verification of Gibbs' theorem. Since the osmotic pressure of a solution is generally difficult to measure, it is simplest to choose a case such that Raoult's law holds good and the concentration of the solution may be used in place of osmotic pressure. The solution should therefore be dilute and should be a true solution: the solute, that is, must be dispersed as simple molecules and not as molecular aggregates like soap micelles. These conditions were obtained by Donnan and Barker (*Proc.*

Roy. Soc. A, LXXXV. 557, 1911), who employed a solution of nonylic acid. Their method of determining Γ was ingenious. A slow stream of air-bubbles was blown up through the solution, and the number and diameter of the bubbles was determined. Adsorption of solute occurred at the surface of each bubble, and the quantity so adsorbed was carried with the bubble into an upper part of the experimental vessel. Diffusion of solute back into the lower portion of the vessel was prevented by suitable baffles and the upper part gradually increased in concentration. If n was the number and r the radius of the bubbles, v the volume of the upper compartment of the vessel in c.c.s and Δc the concentration change in gram-molecules per square centimetre,

$$\Gamma = \frac{v \Delta c}{n \times 4\pi r^2} \text{ grm. mols per cm.}^2.$$

The change of concentration in any experiment was exceedingly small and was calculated by determining the surface tension before and after and comparing the results with a previously determined σ, c curve. Since a large change of surface tension is produced by a very small change in concentration, this is here a very delicate method of quantitative analysis. The following results were obtained:

C (molarity × 10^7)	Γ observed mols/cm.^{2} × 10^{10}	Γ calculated from Gibbs' equation
1·54	6·0	3·5
3·16	9·6	7·2
4·80	6·9	8·0
5·09	5·8	—

A similar experiment with solutions of saponine gave observed values of Γ about three times those calculated from the formula, but the concentration of saponine in true solution is probably very difficult to measure. We can at least say that the adsorption is of the right order as calculated from Gibbs' equation. Errors of uncertain dimensions must have arisen owing to the use of the unsatisfactory drop-number method of determining the surface tension, but the agreement is surprisingly good on the whole.

In earlier experiments by W. C. McLewis and Donnan* the adsorptions of potassium chloride, $BaCl_2$, $CuCl_2$, $AgNO_3$ and caffeine were determined at the interface of water-paraffin oil and for sodium glycocholate, aniline, Congo red and methyl orange at the surface of mercury. The oil and solution were shaken to form an emulsion, the average size of whose particles was measured microscopically, and the surface tension was measured before and after emulsification by the drop-number method. It was assumed that the small amount of oil in the drops which was neither dissolved nor adsorbed would not affect the drop-number: this assumption is probably approximately correct, since suspended solids which are not adsorbed at the surface do not affect the surface tension. An alternative method, which did not involve the difficulty of finding the mean surface of emulsified particles, was to drop mercury through the solution so that the adsorption at the mercury-water interface was determined by what amounted to an inversion of the method of Donnan and Barker: a similar plan has also been used by Patrick who measured the adsorption of $HgNO_3$, salicylic acid, picric acid, neofuchsin, etc., at a mercury interface. Of these cases only aniline and caffeine gave results in approximate agreement with Gibbs' theorem: every other substance showed an adsorption considerably too great, up to one hundred times the calculated value.

It is worth devoting some space to consider the causes of these deviations from the theoretical results of so fundamental a theorem. In the first place the surface tensions were always measured by the drop-volume method, which the subsequent investigations of Harkins have shown to give incorrect results: the errors from this source could however only be a very small fraction of the whole divergence. A much more serious objection, in the case of solutions of substances of high molecular weight, is the difficulty of determining the concentration of the "true" solution. Much of the Congo red, for example, will be in the form of molecular aggregates which, like the oil in an emulsion, are without effect on the surface tension. The true concentration was probably only a fraction of that given by Lewis and Patrick, and the relative changes of concentration would have been correspondingly smaller.

* Lewis, *Phil. Mag.* 1908, 1909.

That is to say that $\frac{d\sigma}{dlnc}$ and therefore also Γ was actually greater than it appeared to be.

Such an explanation cannot however account for the abnormally high values of the adsorption of simple salts at a water-oil interface, as found by Lewis. If we are to accept these results (though the emulsion method is certainly the least satisfactory of those used for the present purpose) some sécondary effect must be looked for, such as the increased solubility of oil in water when emulsified and in the form of small particles. (The mean radius in one experiment was found to be about 4×10^{-5} cms., a size at which Hulett and Ostwald (see page 166) found a notable increase in the solubility of calcium and barium sulphates.) It is probable however that the chief error introduced was the disturbance brought about by the effect on the surface tension of the free charges of the salt ions (Lewis, *Zeit. Physikal. Chem.* LXXIII. 129, 1910). (See Ch. VII.)

A somewhat different means of verifying Gibbs' law may be suggested in connection with the solubility of the higher fatty acids, investigated by Langmuir and Adam (see Chap. III). Here the adsorbed quantity Γ is readily measured and the chief difficulty consists in estimating the very small concentration of solute in the solution. The latter may however be measured by observing the contraction of a relatively soluble film as it dissolves in the underlying water, and the solution so obtained might in some cases be titrated electrometrically.

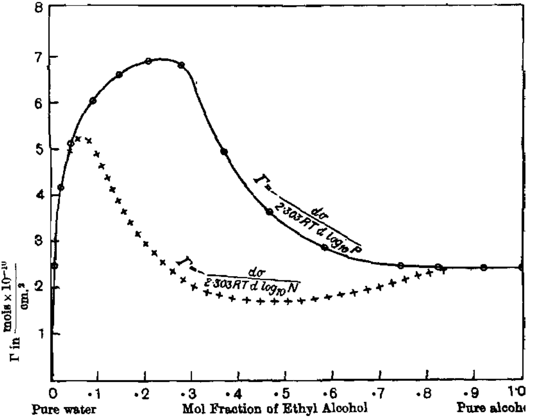
Although absolutely conclusive quantitative evidence for Gibbs' theorem is so far lacking, its qualitative truth is apparent from so many distinct sources that we may build upon it with considerable confidence, and in the remainder of this book it will be treated as a valid principle.

3. The surface tension of solutions.

We would anticipate from a consideration of the Gibbs equation that the addition of a solute to a solvent will cause marked changes in the composition of the surface phase if the solvent and solute possess different surface tensions. On the addition of a highly capillary active material to water the surface phase becomes rich in the solute and the surface tension of the solution will fall rapidly.

These conditions are realisable experimentally with solutions of the higher fatty acids and alcohols with water. The σ, N curve falls rapidly at first and subsequently approaches almost asymptotically a limiting value. With the aid of the Gibbs equation we may readily determine the form of the Γ, N curve, where Γ is the surface excess. The surface concentration may be assumed equal to Γ if we

Surface Excess of Ethyl Alcohol at a surface between air and mixtures of Ethyl Alcohol and Water.



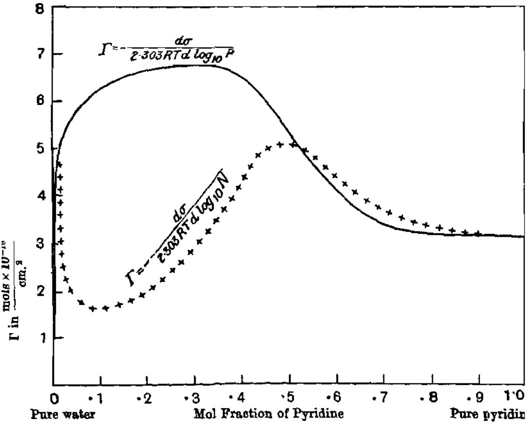
confine our attention to solutes of relatively high capillary activity. Again it is necessary to have information about the thermodynamic concentration or activity of the solute in the solution if the true value of Γ is to be determined.

For dilute solutions of non-ionising or feebly ionising solutes no serious error is introduced by employing bulk concentrations in lieu of activities, but in general serious errors are introduced through failure to take this precaution. The activities may be measured conveniently by means of any of the colligative proper-

ties of the solution, such as the partial vapour pressure, osmotic pressure or freezing point of the solution (see Lewis and Randall, *Thermodynamics*).

The data available for determining accurately Γ, N curves for such binary mixtures over a complete range of concentrations are limited, but the following examples are typical of the general form

Surface Excess of Pyridine at an interface between Mixtures of Pyridine and Water, and Mercury (no charge on surface).

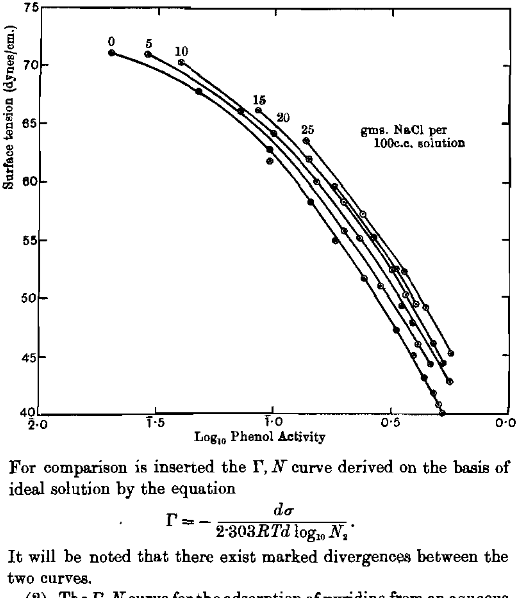


of these curves (*Proc. Roy. Soc.* A, CIX. 57, 1925). The two examples depicted in the curves are (1) ethyl alcohol water mixtures from the surface tension data of Bircumshaw (*J.C.S.* CXXI. 887, 1922) at 25° C. with the corresponding values of the partial vapour pressure of ethyl alcohol intrapolated from the data of Konovalow and Wrensky. By means of the latter the values of $d\mu_2$ are obtainable with the aid of the equation

$$d\mu_2 = 2{\cdot}303RTd\log_{10}fc = 2{\cdot}303RTd\log_{10}P_2,$$

which is nearly exact for the small vapour pressures which these mixtures exert at 25° C. The Γ, N curve (where N is the mol. fraction) is derived from the slope of the $\sigma, \log P_2$ curve by means of the Gibbs equation in the form

$$\Gamma_2 = -\frac{d\sigma}{2{\cdot}303RTd\log_{10} P_2}.$$



For comparison is inserted the Γ, N curve derived on the basis of ideal solution by the equation

$$\Gamma = -\frac{d\sigma}{2{\cdot}303RTd\log_{10} N_2}.$$

It will be noted that there exist marked divergences between the two curves.

(2) The Γ, N curve for the adsorption of pyridine from an aqueous solution at a water-uncharged mercury interface. The surface tension measurements employed are those found by Gouy (*Ann. de Chimie et de Physique*, VIII. ix. 130, 1906), whilst the pyridine activities are derived from the vapour pressure data of Zadwiski

extrapolated to 18° C. For comparison is inserted the Γ, N curve, regarding the pyridine water solution as ideal.

It is important to note that if the mercury surface be charged the extent of adsorption will be very materially affected (see Ch. VII). Lack of this precaution has vitiated the conclusions derived from a number of experiments, see ante, p. 36.

The σ, N curves for the surface tension of phenol in water the activity of which can be varied by the addition of various concentrations of sodium chloride present interesting features (*J.C.S.* CXXVII. 1668, 1925). The surface tensions were determined by the drop weight method whilst the activities were obtained by a partition method utilising paraffin as parting liquid. The parting ratios were calibrated by means of freezing point determinations for pure phenol-water solutions by the metbod of Lewis and Randall. It will be noted that whilst the slopes of the curves for different salt concentrations are identical indicating that for identical bulk activities of phenol the surface concentrations are likewise identical, yet the surface tensions are by no means dependent on tbe surface concentrations of the phenol alone even when this layer is tightly packed, but are affected by the nature of the underlying liquid. (From tbe value of Γ_∞ Å. is found to be 23·8 Å. for phenol on water, in close agreement with that obtained for vertically orientated substituted insoluble phenol derivatives by Adam.)

It will be observed that the Γ, N curves for such binary mixtures follow the same course—a rapid followed by a more gentle rise of Γ as N increases to a well defined maximum followed by a drop and an asymptotic fall in the Γ value. In the case of alcohol water mixtures $\Gamma_{max.}$ is obtained at about 0·3N. To find an adequate explanation for the complete Γ, N curve is by no means an easy matter. It is clear that the first portion of the curve may be taken to represent an increasing surface concentration of alcohol and this proceeds to a limiting value—an observation first made by Milner (*Phil. Mag.* XIII. 96, 1907), who showed that for relatively strong solutions of acetic acid the surface tension of the solutions could be expressed as a function of the concentration of the acetic acid in the following form:

$$\sigma_0 - \sigma = \alpha + \beta \log_{10} N \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1),$$

where σ_0 is the surface tension of water, σ that of the solution, and α and β constants for the particnlar solute employed.

From (1) we obtain by differentiation

$$\frac{d\sigma}{d \log N} = -\beta,$$

and this equation together with that of Gibbs for ideal solutions,

$$\Gamma = -\frac{d\sigma}{2{\cdot}303RTd\log N},$$

leads to the expression

$$\Gamma = \frac{\beta}{2{\cdot}303RT}.$$

Similar conclusions as to the attainment of a finite maximum value of Γ as pointed out by Langmuir (*J.A.C.S.* XXXIX. 1883, 1917) can be obtained from an empiric equation put forward by v. Szyszkowski (*Zeit. Phys. Chem.* LXIV. 385, 1908) in the following form:

$$\frac{\sigma_0 - \sigma}{\sigma_0} = b \log_{10}\left(\frac{N}{N_0} + 1\right),$$

where b and N_0 are constants. If N be large compared with N_0 this equation approximates to that of Milner and

$$\Gamma_{\text{limit}} = \frac{b}{2{\cdot}303RT\sigma_0}.$$

An application of this relation to the data for ethyl alcohol would give a value of Γ corresponding to the maximum of the dotted curve which is evidently not the true maximum. Yet the idea that the excess of solute calculated with the aid of Gibbs adsorptive equation is situated in the outermost layer of atoms which Milner put forward on the strength of the above relation is one which as we shall note in the next section has been reaffirmed by Langmuir. Liquids which mix in all proportions and whose surface tensions in the pure state do not differ greatly frequently give Γ, N which are nearly straight. In some cases, such as in mixtures of carbon disulphide and dichlorethane, the addition of one liquid to the other produces a lowering of the surface tensions; thus on a carbon disulphide rich bulk phase dichlorethane is positively adsorbed and vice versa, the σ, N curve thus going through a minimum (at *ca.* equimolecular proportions, Whatmough). For the inorganic salts dissolved in water and alcohol the surface tension is raised, the surface phase is richer in water than

the bulk phase and the increase in surface tension thus produced is nearly proportional to the salt concentration.

In rare cases—such as sulphuric acid and water—a surface tension maximum mixture is obtained (44 °/₀ H_2SO_4, Morgan).

Limitations imposed by the limits of mutual solubility of the liquids in the bulk phase in general however preclude examination of the σ, N curves over a wide range of concentrations.

We have noted that the Gibbs equation permits us to calculate the composition of the surface phase from a knowledge of the σ, N curve and the "activity" of the solute in the solution; it does not however give us any information as to the thickness of the phase, beyond an indication that the liquid above the geometrical dividing surface is uniform in composition and does not acquire the characteristics of a phase in bulk. In the next chapter our attention will be devoted to the behaviour of films of insoluble substances on the surfaces of liquids and we shall have occasion to observe that we possess almost conclusive evidence that the surface phases of such films are but one molecule thick and further that the molecules of the insoluble material adsorbed on the liquid are orientated in a vertical plane; being attached to the liquid surface in the case of a complex molecule by some particular group or groups.

These conclusions indicate that the Gibbs film, for such systems at any rate, is but one molecule thick and it is evidently important to consider how far we are justified in making the assumption that in all cases both for pure liquids and for solutions the Gibbs layer may be considered as similar in character, viz. unimolecular in thickness and consisting of orientated or partially orientated molecules.

It has already been observed in the case of pure liquids such as substituted hydrocarbons that the surface tension was, if not completely defined by the *non-polar portions of the molecule*, at least not so markedly affected by substituent groups as we should anticipate if no orientation existed. Again, although vaporisation and condensation at a liquid surface such as water at high temperatures takes place with great speed, yet the life of a molecule on the surface is probably long enough to permit of such adjustment as orientation requires. Even more conclusive in favour of the hypothesis of at least partial orientation is the evidence derived from a consideration of the latent heats of evaporation and the

divergences noted in the Eötvös constant for unsymmetrical undissociated molecules.

For mixtures of substances of markedly different surface tensions also we have noted that over a considerable range of concentration the Gibbs film appears to behave as if it were unimolecular in character, but for strong solutions of these substances as well as for mixtures of liquids of similar surface activities the evidence for such a restricted film thickness is by no means so conclusive. It must indeed ratber be assumed that in these cases the application of the principle of minimum surface energy to mixtures somewhat similar in internal pressure leads to the formation of a diffuse layer in which the composition varies possibly in an exponential manner with the depth. The top layer alone may be said to be formed by the operation of chemical forces.

Thus in the case of concentrated solutions of ethyl alcohol in water the subsequent decrease in Γ with increasing values of N might on the assumption of an orientated layer of alcohol molecules in the Gibbs film, be accounted for by a decrease in orientation when the more polar and presumably stronger water in the bulk phase is replaced by the weaker alcohol. Alternatively however the fall in Γ need not necessarily involve a rearrangement in the outermost layer of molecules. This is shown by the following considerations: in applying the Gibbs equation we have drawn our arbitrary dividing surface in such a position that the solution below it is uniform in composition as a whole. If for example in alcohol rich solutions water molecules were adsorbed to the hydroxyl groups of the orientated alcohol molecules in the Gihbs layer, the alcohol rich phase would lie just above a water rich phase. The result of such adsorption below the surface would be that our dividing surface would be raised so as to include some of the alcohol rich phase to compensate for the excess of water just below it. These considerations indicate at least that it is a difficult matter to draw any conclusions as to the nature of the Gibbs film from information provided by the second portion of the Γ, N curve. But the fact that the change in surface tension from $N=0{\cdot}3$ to $N=1$ is only 6·0 dynes per cm. as against 44 dynes per cm. for the rest, tends to support a theory which does not involve any fundamental rearrangement of the *surface* layer in this region.

For the initial portion of the curve however we may conclude with some degree of assurance that the Gibbs film may attain a finite saturation value for the solute and does not become progressively thicker on increasing the concentration in the bulk phase.

4. The Unimolecular Gibbs Layer.

Langmuir from his study of the films of insoluble substances upon water (see Ch. III) concluded that the film was in these cases but one molecule thick and that the molecules in the film were definitely orientated.

He suggested that in all cases for both soluble and insoluble substances and for pure liquids the Gibbs film might be regarded as but one molecule thick and consist of pure solute molecules for substances which lower the surface tension of the solvent. If Γ be the surface concentration in grm. mols per sq. cm., on the hypothesis of a unimolecular layer of molecules we obtain $A = \frac{1}{\Gamma}$ as the area in sq. cms. per grm. mol. or $\frac{1}{\Gamma N} = a$ as the area occupied by one molecule of the solute in the unimolecular Gibbs film.

In the following table are given the limiting values of A calculated from Milner's and v. Szyszkowski's equations by Langmuir and Harkins.

Acid. No. of carbon atoms in chain	Area in Å.
1	57
2	50
3	39
4	36
5	32
6	31
7	34
8	—
9	32
10	31

Langmuir considered these values to be "in substantial agreement with the value of A (25 Å.) found for insoluble films," though the discrepancy cannot be attributed to experimental error.

If we apply this hypothesis of the unimolecular character of the

Gibbs film to our observed value of $\Gamma_{max.}$ for alcohol water mixtures we obtain an area per molecule of 24 Å. as compared with a value of $A = 33$ Å. obtained with the aid of Milner's equation.

The application of the gas laws to surface films.

In the previous sections we have noted that the hypothesis of a unimolecular Gibbs layer for solutions of liquids of markedly different internal pressures together with the equation of Gibbs leads to values for molecular areas and thicknesses which are not at all unreasonably different from those determined by means of X-ray measurements, or from a study of insoluble substances on the surface of water, but cannot be said to be identical within the limits of experiment. In one respect, however, such soluble films differ from the insoluble films which we shall have occasion to examine in the next chapter; the surface tension of solutions which according to the Gibbs adsorption equation

$$\Gamma = -\frac{N}{RT}\frac{d\sigma}{dN} \quad\text{.........................(1)}$$

have a value of $\Gamma = 2 \times 10^{-10}$ mols per sq. cm. give values of $\sigma_0 - \sigma$ which vary from 5 to 10 dynes per cm. at 20° C. The same number of molecules of palmitic acid put on a sq. cm. of water surface would not affect the surface tension of water by so much as one-tenth of a dyne.

Soluble substances appear to be capable of occupying enormous areas of the water surface and to be still capable of affecting the surface tension.

To explain this phenomenon Langmuir resuscitated a theory of Traube (*Lieb. Ann.* CCLXV. 27, 1891). The latter found that the quantity F, or the surface tension lowering, defined by

$$F = \sigma_0 - \sigma,$$

is approximately proportional to the bulk concentration for small values of F or

$$F = kN.$$

If the solution be regarded as ideal this combined with (1) gives

$$F \cdot \frac{1}{\Gamma} = RT \quad \left(\text{since } \frac{d\sigma}{dN} = -\frac{dF}{dN} = -k\right)$$

or $$FA = RT.$$

The resemblance between this equation and the equation $PV = RT$ for perfect gases led Traube to suggest that the lowering of the

surface tension of a solvent by a solute is due to the thermal agitation of the solute molecules adsorbed at the surface. The observed surface tension is on this view the resultant of two forces, one the unaltered tension of the solvent σ_0 and the other an outward two-dimensional "gas" pressure exerted by the solute molecules in excess at the interface. According to Langmuir the failure of insoluble films to show this "gas" pressure is due to the considerable lateral attraction between hydrocarbon chains sufficiently long to cause insolubility, in consequence of which these films resemble liquids rather than gases. The possibility of the existence of films showing properties resembling the three states of matter had previously been suggested by Devaux (see Ch. III).

Langmuir adds that "surface liquids" may exert a "vapour pressure," though this is less than 0·5 dyne per cm. in all insoluble films so far investigated. We have noted that Traube's equation $F = kN$ does not obtain except for extremely small values of F, an observation which led Milner and v. Szyszkowski to develope the alternative empiric relationships between F and N already alluded to. If however we accept the hypothesis that we may apply a kinetic theory of surfaces for soluble substances in the unimolecular Gibbs film containing adsorbed solute molecules, it is clear that these adsorbed molecules can hardly be expected to behave like perfect gases where molecules are supposed to be infinitely small compared with the free space separating them. For at all but the smallest values of F the area per mol. A is not much greater than the least area A_0 which a mol. can occupy under high compression. It is therefore unreasonable to expect $\frac{FA}{RT}$ to be unity when $\frac{PV}{RT}$ for a real gas would not be. The values of $\frac{FA}{RT}$ over a range of values of F may conveniently be obtained by slightly transforming Gibbs' equation in the following manner.

Since
$$dF = \Gamma d\mu,$$
$$A = \frac{d\mu}{dF},$$
whence
$$\frac{FA}{RT} = \frac{d\mu}{RT}\frac{F}{dF} = \frac{d\mu}{2{\cdot}303RT}\frac{1}{d\log F}.$$

If the solution be ideal

$$d\mu = 2{\cdot}303 RT\, d\log_{10} c,$$

whence
$$\frac{FA}{RT} = \frac{d\log c}{d\log F}.$$

The data of v. Szyszkowski have been employed for determining the values of $\frac{FA}{RT}$* for butyric, valeric and caproic acids shown in the curves on p. 49.

In the case of soluble substances of low capillary activity the evaluation of $F = \sigma_0 - \sigma$ is a matter of some difficulty, for this two-dimensional pressure must be regarded as the difference in surface tension between that of the liquid without the Gibbs film and one in which the Gibbs film is established; only as a first approximation may the ideal dynamic surface tension of a solution, i.e. of a solution without a Gibbs film, be regarded as equal to the surface tension of the solvent.

The *resemblance between these curves and the corresponding* curves for a gas like nitrogen is most marked. The initial dip in

* For weak electrolytes the degree of dissociation found by the freezing point method agrees with that found from conductivity within the limits of experimental error and Ostwald's dilution law is obeyed.

When the concentration c of a solution changes, the change in potential of the water is given by

$$d\mu_1 = -\frac{RT}{55{\cdot}51}\, d\,[c\,(1+a)],$$

55·51 being the number of mols in 1000 grms. of water.

The corresponding change in the potential of the solute is

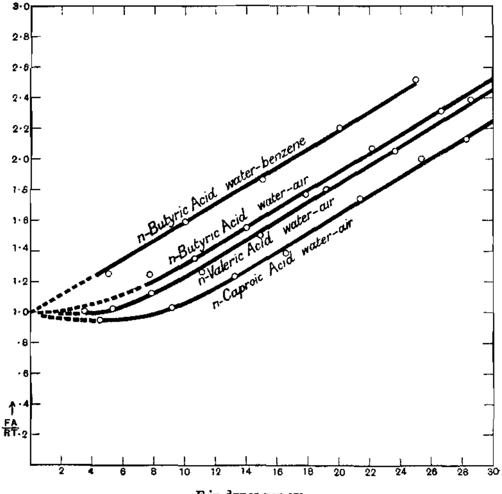
$$d\mu_2 = -\frac{N_1}{N_2}\, d\mu_1 = -\frac{55{\cdot}51}{c}\, d\mu_1 = RT\,\frac{d\,[c\,(1+a)]}{c} = RT\left[\frac{dc}{c} + \frac{a\,dc}{c} + da\right].$$

Integrating this we obtain

$$\frac{\Delta\mu_2}{2{\cdot}303RT} = \Delta\log fc = \Delta\log c + \int_c^{c+\Delta c} a\, d\log c + \frac{\Delta a}{2{\cdot}303}.$$

The definite integral may be evaluated if a does not exceed 0·1 by means of Ostwald's dilution law $a^2c = K$. For $d\log c = -2d\log a = -\frac{2da}{2{\cdot}303}$. The last two terms which give the value of $\Delta\log f$ thus reduce to $-\frac{2\Delta a}{2{\cdot}303a} + \frac{\Delta a}{2{\cdot}303a} = -\frac{\Delta a}{2{\cdot}303a}$, whence $\Delta\log f = -0{\cdot}4343\Delta\sqrt{\frac{K}{c}}$. K for the higher fatty acids determined by conductivity measurements is $1{\cdot}5\times10^{-5}$.

the curve becomes more marked as the length of the hydrocarbon chain increases, whilst for large F values the slight negative curvature obtained for gases is faithfully reflected.



For the regions of high pressure Amagat proposed the equation

$$\frac{PV}{RT} = \frac{Pb}{RT} + x$$

to represent the behaviour of gases, an equation in which b is a constant for any one gas and represents the least volume the gas can occupy at these temperatures. On the other hand x varies both with the nature of the gas and with the temperature, always approaching unity for very high temperatures and becoming

smaller as the temperature approaches the critical temperature. A corresponding equation

$$\frac{FA}{RT} = \frac{FB}{RT} + x,$$

in which B is the limiting area, and $\frac{1}{x}$, a measure of the lateral molecular cohesion, will therefore represent the behaviour of surface films for all but the smallest values of F. The values of B and x for substances studied by v. Szyszkowski are given in the following table to which has been added the values for butyric acid at a water-benzene interface found from the measurements of Harkins and King (*J.A.C.S.* XLI. 986, 1919) and those for substances adsorbed at a water-mercury interface examined by Gouy.

Substance	*Interface*	B Å. per molecule	x	*Observer*
n-Butyric acid ...	Water-air	24·3	·73	von Szyszkowski
n-Valeric acid ...	"	24·3	·63	"
n-Caproic acid ...	"	24·3	·43	"
Iso-butyric acid ...	"	25·1	·78	"
Iso-valeric acid ...	"	25·1	·68	"
Iso-caproic acid ...	"	25·1	·48	"
Iso-amyl alcohol ...	"	—	·59	"
n-Butyric acid ...	Water-benzene	24—25	1—·95	Harkins and King
Tertiary butyl alcohol	Water-mercury	24·0	·52	Gouy
" amyl "	"	28·0	·46	"
Cane sugar	"	72·7	1·0	"
Pyridine	"	26·0	1·0	"

All the normal acids show practically the same value of B at a water-air interface, a value which gives the mean area per molecule of 24·3 ± 0·3 Å. This value is also given by n-butyric acid at a water-benzene interface. The values of B for the iso-acids are consistently a little larger than those for the normal acids. The values of x show that these acids resemble gases whose critical temperatures increase as the carbon chain lengthens. The iso-

acids have slightly larger values of x than the corresponding normal acids, indicating a decrease in the lateral cohesion between chains when branched.

It is interesting to note the large value of x for butyric acid at a water-benzene interface. Immersion of the hydrocarbon chains in benzene appears to decrease the attraction between the hydrocarbon chains.

This equation leads to a new relation between F and c, for, on eliminating A by means of the Gibbs equation we obtain

$$\frac{\mu_2 - \mu_1}{2{\cdot}303RT} = x \log F + \frac{B}{2{\cdot}303RT} F,$$

or

$$\log fc + K = x \log F + \frac{B}{2{\cdot}303RT} F,$$

an equation which is found to give results which agree remarkably well with the precise surface tension measurements of von Szyszkowski.

Adsorption of electrolytes.

In many cases such as at water-mercury interfaces electrolytes are positively adsorbed. The application of the kinetic theory to surface films of molecules leads, as we have seen, to a ready interpretation of the lowering of the surface tension by capillary active nonelectrolytes. For electrolytes an additional factor has to be considered, namely the mutual interaction of the electrically charged ions adsorbed. As we shall have occasion to note the distribution of the adsorbed ions, both positive and negative, at an interface such as water-mercury is not readily determined, but it is clear from a consideration of the data of Gouy that mutual ionic electrical repulsion in the interface is an important factor. In the case of potassium iodide, for example, for very small values of F the Traube relationship

$$F = 2\Gamma RT$$

is obeyed (each molecule of KI yields two ions, thus the number of individuals in the surface phase is 2Γ). As F increases, instead of $\frac{FA}{RT}$ passing through a minimum, as is the case where molecules possess a certain lateral cohesion, the value of this quantity rises

rapidly, indicating that a repulsive action of great magnitude is becoming operative as the superficial concentration increases. The nature and structure of this double layer so produced will be discussed in a later section.

Surface Pressures.

In many cases the corresponding two-dimensional pressures for surface films may be evaluated by comparing the behaviour of a surface film with that of a gas or solution in the same condition, i.e. possessing the same value of x. Thus in the case of cane sugar ($x = 1$) the data of Gouy provide us with information on the surface tension of the interface water-mercury in the presence of varying concentrations of cane sugar, whilst we can, from the data of the Earl of Berkeley and Hartley on the osmotic pressure of cane sugar solutions ($x = 1$), evaluate the activity of such solutions with the aid of the equation $\frac{d\mu}{2{\cdot}303RT} = d \log \pi$.

For an aqueous solution at 0° C. showing an osmotic pressure of one hundred atmospheres we find $\frac{\pi}{CRT} = 2{\cdot}3$, whilst $\frac{FA}{RT}$ has this value when the surface phase acquires an F value of 6·8 dynes per cm. (at 18° C.). It is evident that each dyne per cm. of F corresponds to nearly 14·7 atmospheres osmotic pressure, so that the "surface pressure" at a mercury interface, the surface tension of which has been lowered 30 dynes by cane sugar, is equivalent to an osmotic pressure of 440 atmospheres.

The ratio P/F is evidently equal to B/b when expressed in absolute units. Under high pressures at 0° C. the value of b for nitrogen is 30·5 c.c. per mol. n-butyric acid at a water-air interface may be compared to nitrogen at 0° C. between the pressures 400—1500 atmospheres, since $x = 0{\cdot}73$ for both substances. B for butyric acid $= 1{\cdot}49 \times 10^9$ sq. cm. per mol., hence

$$\frac{P}{F} = \frac{1{\cdot}49 \times 10^9}{30{\cdot}5} = 4{\cdot}82 \times 10^7.$$

Thus a surface pressure of one dyne per cm. is equivalent to a pressure of $4{\cdot}82 \times 10^7$ dynes per sq. cm. or 47·7 atmospheres.

The surface tension of solutions and chemical constitution.

Langmuir has pointed out that some important conclusions may be drawn from consideration of the surface and bulk concentrations of capillary active substances.

The diminution in potential energy of a molecular species when it passes from one phase in which it has a concentration c_1 to that of another phase of concentration c_2, with which it is in equilibrium, may probably be represented by an equation of the Boltzmann type

$$\frac{c_2}{c_1} = Ke^{-\frac{Q}{RT}},$$

where Q is the decrease in potential energy accompanying the change. With this assumption a value of the relative polarity of different groups from a measure of the decrease in potential energy of the molecule as it passes from the interior to the surface phase may be obtained.

From a knowledge of the surface and bulk concentrations of various organic substances in dilute aqueous solutions, Langmuir has calculated the following values.

Group	*Loss of potential energy in* passing from the interior of the liquid to the surface, in calories per grm. mol.
$-CH_2-$	710
Primary OH	570
Tertiary OH	950
Monobasic acids ...	473
Ester	470
Ketone	295
Aldehyde	210
Amide	−510
Primary amine ...	600
Dibasic acid } " alcohol } ...	−700
Double bond	−400
—OH in an acid ...	−800

It is interesting to compare the values of Q thus determined for a series of solvents of varying internal pressure (cf. Hildebrand, *Solubility*, p. 116). The magnitude of the departures from Raoult's law of ideal solution vary in a manner which is highly significant as the Q values of solvent and solute diverge from one another.

We note also that each CH_2-group in a hydrocarbon chain is similar in character to each other, i.e. the loss of potential energy for a CH_2-group on passing to the surface is identical irrespective of its position in a chain.

5. Negative Adsorption.

The inorganic salts raise the surface tension of water and in accordance with the thermodynamic considerations implied in the Gibbs equation, the surface concentration of solutions must be less than the bulk concentration.

The experimental data on the subject of the surface tensions of such solutions is scanty. The early work of Valson (*C.R.* LXXIV. 103, 1872) and of Morgan (cf. *J.A.C.S.* XXXV. 1753, 1913) cannot be considered as reliable. More accurate appear to be the data of Stocker (vibrating jet) (*Zeit. Phys. Chem.* XCIV. 149, 1920), who compared his values with those of Grabowski and Pann (*Diss.* Königsberg, 1904) (capillary rise) and Sentis (hanging drops) (*Thèse*, Paris, 1897).

Over a considerable range of concentration the results were found to be capable of expression by a linear formula

$$\sigma_{\text{solu.}} - \sigma_{\text{water}} \text{ or } F = Km,$$

where m = mols of salt per 1000 gms. of water.

The surface tension concentration curves were found however to be slightly convex towards the concentration axis, a curvature becoming more pronounced for strong solutions.

The comparison of the values of K obtained by these observers for various salts reveals the fact that marked variations exist. *A few such values are given in the following table.*

Salt	K		
	Grabowski and Pann	Sentis	Stocker
$NaCl$ ...	1·60	1·66	1·63
KCl ...	1·33	1·40	1·43
$CaCl_2$ ...	3·64	3·56	2·98
Na_2SO_4 ...	1·92	2·88	3·13
K_2SO_4 ...	2·54	2·63	3·52

Goard has determined the surface tensions of a few salt solutions by the drop weight method; employing the method of Iredale for calculating the surface tension, the following values were obtained.

Salt	Mols per litre	σ_{20}	Salt	Mols per litre	σ_{20}
LiCl ...	0	73·08	$CdCl_2$ ...	0	73·08
	1·08	74·74		0·471	74·04
	1·94	76·22		0·942	74·67
	3·51	79·46		2·36	76·80
				3·49	79·20
NaCl ...	0	73·08		4·71	82·10
	1·00	74·78			
	2·00	76·51	$AgNO_3$	1·00	74·37
	3·22	78·73		2·00	75·23
	5·00	82·20		3·00	75·94
				5·00	77·69
KCl ...	0	73·08			
	1·00	74·55			
	2·00	76·13			
	3·00	77·77			
	3·80	79·17			

It is interesting to observe, that with both $CdCl_2$ and $AgNO_3$ the curve is initially concave to the concentration axis and that there occurs with increasing concentration a point of inflexion, after which the convex type of curve obtained with the simple completely dissociated salts appears.

On the assumption of the unimolecular character of the Gibbs film we can, as Langmuir has indicated, obtain some idea as to the size of the solvent molecules. If the thickness of the film be τ and the bulk concentration C, the quantity of solute which has left the film, on the hypothesis of a unimolecular film of pure solvent existing at the surface, will be $C\tau$; this is equivalent to the negative surface excess or

$$C\tau = \Gamma = -\frac{d\sigma}{d\mu}.$$

The thickness of the adsorbed layer is thus $\dfrac{1000\dfrac{d\sigma}{d\mu}}{M}$.

Langmuir obtained a value of $\tau = 4$ Å. for the thickness of a water molecule in the surface of a solution of potassium chloride. From a knowledge of the molecular volume we obtain a cross-

sectional area of *ca.* 7 Å. This calculation therefore involves a conception of an elongated water molecule whose diameter is about two-thirds of its length orientated vertically at the surface. Using Cederberg's values for the elevation of the surface tension of alcohol by dissolved salts (*J. Chem. Phys.* IX. 10, 1911), Langmuir obtains $\tau = 4{\cdot}4$ Å. and $A = 22$ Å., a value in good agreement with that calculated by other methods, viz., 24 Å. (see *ante*). From a knowledge of the activity data of the salts (Harned, *J.A.C.S.* XLIV. 252, 1922), Goard has calculated the values of Γ over an extended range of concentration and finds that Γ is not independent of the concentration.

The film thickness calculated from Γ would appear to vary with the concentration of the salt as indicated by the following data in which the negative adsorption in gm. mols per sq. cm. and the thickness of the layer τ in Å. are given.

Salt molarity	LiCl		NaCl		KCl	
	$\Gamma \times 10^{11}$ mols per sq. cm.	τ	$\Gamma \times 10^{11}$ mols per sq. cm.	τ	$\Gamma \times 10^{11}$ mols per sq. cm.	τ
0·1	0·55	5·5	0·60	6·0	0·40	4·0
0·2	1·05	5·25	1·15	5·75	0·83	4·2
0·5	2·10	4·25	2·30	4·7	2·15	4·4
1	3·19	3·2	3·65	3·75	3·75	3·85
2	4·63	2·3	5·9	3·05	6·10	3·25
3	5·90	2·1	7·6	2·7	8·05	2·95
4	—	—	9·35	2·55	9·8	2·75
5	—	—	11·0	2·45	—	—

The limiting values of τ are found to vary with the nature of the salt, the following data being obtained.

Salt	$\tau_{min.}$ in Å.
$CdCl_2$ ...	3·9
$AgNO_3$ ...	2·8
LiCl ...	2·0
NaCl ...	2·3
KCl ...	2·6

These values are much smaller than those calculated by Langmuir from somewhat scanty data and indicate that our conception of a

layer of orientated solvent molecules existing at the surface must be modified.

It is interesting to note that the ionic mobilities lie in the order $\dot{\mathrm{K}} > \dot{\mathrm{Na}} > \dot{\mathrm{Li}}$, whilst the true ionic radii are in the inverse order (Born, *Zeit. f. Physik*, I. 221, 1920). It is probable that the hydrated ions are always present in the surface but not necessarily in equal amounts, and that as the difference in concentration between surface and bulk phases increases this is accompanied by a simultaneous increase in the steepness of the concentration gradient from surface to bulk phase, a process which may be associated with the removal of water of solvation from around the ions.

Some further insight into the behaviour of salts at air-liquid interfaces may be obtained from a consideration of the electrification produced at such surfaces by solution of salts in the liquid, a point which will be considered in Ch. VII.

6. *The adsorption of gases on liquid surfaces.*

Very little accurate information is at present available on the adsorption of vapours and gases on liquid surfaces. Iredale (*Phil. Mag.* XLV. 1094, 1923; XLVIII. 175, 1924), however, has studied the adsorption of a number of vapours at a mercury surface. The experimental data have led to a number of interesting conclusions.

The surface tension of mercury in the presence of the vapour at various partial pressures was measured by the drop weight method. The following values were obtained for the surface tensions of mercury in the presence of vapours of methyl acetate, water and benzene at various partial pressures at 26—27° C.

Methyl acetate		Water		Benzene	
Partial pressure mm.	σ	Partial pressure mm.	σ	Partial pressure mm.	σ
0	472	0	472	0	472
19	444	11·6	461	26·5	415
109	423	17·5	454	37·0	410
137	419	25	447—368	42·1	406
157	418			49·9	402
227	417			61·8	400
Sat.	412—370			76·3	396
				101·0	395—354

It will be noted that the fall in surface tension of the mercury with increase in the partial pressure of the vapour is similar to the fall observed in aqueous solutions with increase in concentration of a capillary active solute.

The vapours are evidently adsorbed on to the mercury surface and the amount adsorbed can be calculated with the aid of the Gibbs equation

$$\Gamma = -\frac{d\sigma}{d\mu},$$

where $d\mu = 2{\cdot}303RT\,d\log_{10}P$.

Calculating the maximum amount of each vapour adsorbed we obtain for the limiting molecular area from the relationship $\Gamma = \frac{1}{A}$, the following values:

	Limiting area in Å.
Methyl acetate ...	27
Water	16
Benzene	21

which are in fair agreement with those calculated from the surface tension of solutions and indicate that in the adsorption of these vapours on mercury we are, in all probability, dealing with the formation of a unimolecular orientated adsorption film of vapour. It is further interesting to note that the transition from a primary adsorption film to a system in which the liquid is condensed on the mercury surface in the form of a thick layer, the free surface of which would possess the properties of the free surface of the liquid in bulk, is not abrupt. We note that a point of instability is reached when the vapour pressure approaches saturation value and that the apparent surface tension of the drop can fluctuate within relatively wide limits. Iredale has shown that these values do not correspond to the tensions mercury/liquid, liquid/air, but are due to a condensed film, a secondary film on the mercury surface. Whilst the transition from the primary film to the thick layer through the formation of secondary layers (Hardy, *Proc. Roy. Soc.* LXXXVIII. 316, 1913) takes place in this particular case within narrow limits of vapour pressure change, there is little doubt

from the data that the change is definite, or that the secondary film must be built up from a great number of layers before we arrive at a film with the properties akin to those on the free surface of the liquid. This continuous change in the P, σ curves obtained by Iredale near the critical point $P_{sat.}$ appears to be similar in character to the changes, observed by Goard and Rideal, occurring in the activity, σ curves for phenol water and salt mixtures near the salting out point, and may be taken as evidence for a progressive thickening of the capillary layer before it acquires the properties of a bulk phase.

That adsorption occurs with great ease on mercury surfaces is demonstrated by the wide variations observed in the literature for the surface tension of this substance in contact with various gases. Thus Meyer obtained by the vibrating jet method the following values:

Gas	σ_{18}
CO_2 ...	487
N_2 ...	495
O_2 ...	505
H_2 ...	554

whilst Schmidt obtained by the same method a value of 435·6 for the surface tension of mercury against its own vapour. Harkins by the static method obtained a value of 477 dynes. Similar conflicting evidence is noted in the observations of Stockle (*Wied. Ann.* LXVI. 499, 1898) and Harkins and Ewing (*J.A.C.S.* XLII. 2539, 1920) and Hogness (*J.A.C.S.* XLIII. 1621, 1921). The former obtained values for σ higher in gases than in vacuo, whilst the latter experimenter could detect no difference when gases were admitted.

Iredale obtained the following values in dry air at various pressures:

Pressure mm.	Temp. 18° σ
10^{-5}	475
10^{-4}	410
24	420
130	440
763	456

According to Iredale the true surface tension of mercury in contact with its own vapour at 18° is *ca.* 476 dynes per cm., and that normally there exists some material which rapidly lowers the tension, presumably by adsorption. On increase of the gas pressure however, this material is displaced from the mercury surface and the surface tension rises again *.

Some further insight into the nature of the adsorption layer on liquid surfaces may be obtained by consideration of the phenomenon of the spreading of a volatile substance such as benzene on a limited area of water surface. The conditions of surface spreading necessitate (as we shall note) that the surface tensions of the pure liquid benzene σ_B and of water σ_A together with that of the interface σ_{AB} shall be so related that,

$$\sigma_A > \sigma_B + \sigma_{AB}.$$

If the drop of benzene be previously saturated with water this wet benzene will spread if

$$\sigma_A > \sigma_B' + \sigma_{AB},$$

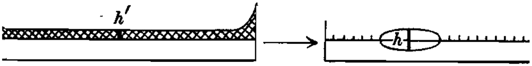
where σ_B' is the surface tension of wet benzene.

The following values are obtained

$$\sigma_A = 72{\cdot}05, \quad \sigma_{AB} = 34{\cdot}68,$$
$$\sigma_B = 28{\cdot}17, \quad \sigma_B' = 27{\cdot}90,$$

indicating that benzene will readily spread on water. It must however be noted that benzene may likewise spread on surfaces by a process of evaporation and condensation (see p. 66).

It is noted that if a layer of benzene be poured on to a limited area of water and the benzene be permitted to evaporate, when a critical thickness of the layer is obtained, h', a sudden rupture occurs and the benzene collects into a number of flat lenses each



of thickness h on the surface. If evaporation of the benzene be

* This explanation advanced by Iredale cannot be considered as adequate or even thermodynamically possible. The change in density of the mercury vapour at the surface of the drop due to retardation of diffusion by the gas admitted, as well as alteration of the orientation of the surface layers may prove important factors.

stopped these lenses will coalesce to a single large lens of thickness h surrounded by an area of water covered with a very thin layer of benzene.

The thickness of the lens h is independent of its area beyond certain small limits of lens area, but the limiting continuous film thickness h' is determined by the nature of the vessel (being dependent on the adhesion of the ring of benzene to the vessel edge) and the rate of evaporation*. It is clear that the solution underneath is saturated with benzene so that the vapour pressure of benzene above the lens must be identical with that above the thin layer. In the case of the spreading of insoluble oils on water we shall have occasion to note that the thin layer in equilibrium with a lens of an oil, such as oleic acid, is unimolecular in character and it is natural at first sight to anticipate that the thin layer of benzene in equilibrium with the lens on the water surface is likewise unimolecular.

Apart from the fact that the layer is very thin and that its vapour pressure is equal to that of the wet lens, no definite information is available on this point. On the other hand, in the case of ethyl alcohol, acetic and the lower fatty acids, we have noted already that a tightly packed unimolecular layer is readily obtained long before the vapour pressure above the solution is equal to that of the pure alcohol (since $\Gamma_{max.}$ is obtained in this case at 0·3 molar) or acid. Thus for these substances to obtain equality of vapour pressure between a surface and bulk phase, layers more than one molecule thick must be necessary.

Spreading may occur by a process of surface solution or by vaporisation from the lens and condensation on the water surface. This latter, indeed, is the only method of spreading on a solid. The adsorption of vapours from a liquid onto a second liquid surface to the point of equilibrium results in the formation of a primary (unimolecular) film and this is doubtless followed in many cases by secondary film formation or a banking up of the layers on the primary film to a thickness which may be several hundred molecules thick. The conditions which have to be fulfilled are two:

(1) the surface tension of the film whether primary or secondary σ_ϵ must attain the value

$$\sigma_\epsilon = \sigma_A + \sigma_{AB},$$

* See p. 97.

(2) the vapour pressure over the film whether primary or secondary must be equal to that over the free surface of the spreading liquid.

If the film be primary or unimolecular in character the vapour pressure is directly related to the surface tension of the solution, for the amount of surface covered θ is proportional to the amount adsorbed or $\theta = K\Gamma$. Evaporation takes place from this covered portion at a rate proportional to the area so covered or $\frac{dx}{dt} = \nu K\Gamma$, where ν is the specific rate of evaporation. Condensation only occurs on the uncovered portion, at a rate proportional to the vapour pressure of the liquid being adsorbed in the vapour form or

$$\frac{dx'}{dt} = K'p(1 - \theta).$$

At equilibrium these two reactions proceed at the same speed or

$$K'p = \frac{\nu K\Gamma}{1 - K\Gamma}.$$

If the specific rate of evaporation ν be very small and p large, evidently multimolecular layers or secondary film formation may readily be obtained.

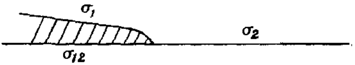
In the case of the adsorption of benzene vapour by mercury examined by Iredale (p. 57); at a pressure of 12·5 mm. at 300° K., 0·564 of the surface is covered with benzene and 0·436 is bare. From the Herz-Knudsen equation it can be calculated that $0{\cdot}902 \times 10^{-3}$ gm. mols of benzene hit this bare surface per second, whilst on the covered surface $0{\cdot}443 \times 10^{-9}$ gm. mols are present. Thus the life of a benzene molecule on the mercury surface is $4{\cdot}9 \times 10^{-7}$ seconds. Over a free benzene surface, if the orientation of the molecules be similar to that on mercury, $1{\cdot}656 \times 10^{-2}$ gm. molecules evaporated per second or the life of a benzene molecule on a benzene surface is $4{\cdot}7 \times 10^{-8}$ seconds.

CHAPTER III

THE SURFACE FILMS OF INSOLUBLE MATERIALS

1. Introduction. Conditions of spreading of non-volatile substances on liquids.

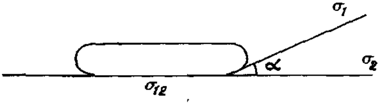
If a drop of oil be placed upon the surface of a liquid in which it is insoluble there will exist at the moment of contact an unstable system in which three surface forces are operative at three interfaces as indicated in the diagram.



We will define by σ_1, σ_2 the two liquid-air and σ_{12} the liquid-liquid interfacial surface tensions. If $\sigma_1 + \sigma_{12} = \sigma_2$, it is evident that the system will be in equilibrium, as no decrease in the free energy of the system can take place by spreading or contraction of the drop. On the other hand if

$$\sigma_1 + \sigma_{12} > \sigma_2$$

a decrease in free energy of the system can take place on contraction of the drop exposing a greater liquid-air interface for the second liquid. The edges of the drop then contract and the flattened drop of liquid assumes the shape of a lens forming a re-entrant angle with the liquid.



The conditions of equilibrium finally attained by the lens of the non-spreading liquid on the surface will be expressed by the equation

$$\sigma_1 \cos \alpha + \sigma_{12} = \sigma_2,$$

an expression first obtained by Neumann.

A third possibility evidently exists when the magnitudes of the three surface tensions involved are as follows:

$$\sigma_1 + \sigma_{12} < \sigma_2.$$

Under these conditions the oil will spread over the surface of the liquid.

The decrease in free energy taking place when the oil spreads over an area of one sq. cm. is evidently $\sigma_2 - \{\sigma_1 + \sigma_{12}\}$ and may be taken as a measure of the tendency of the oil to spread, a point first noted by W. B. Hardy and to the value of which the name "spreading coefficient" has been applied by Harkins.

In the following table are given a few values, chiefly from the data of Harkins, of the spreading coefficients for a number of liquids which spread upon water and for liquids which do not spread but form lenses, in this latter case the value of $\sigma_2 - \{\sigma_1 + \sigma_{12}\}$ is evidently negative.

Spreading liquids		Lens forming liquids	
Liquid	Spreading coefficient	Liquid	Spreading coefficient
Octane	0·22	Carbon disulphide ...	− 6·94
Benzene	8·94	Bromoform	− 9·58
Chloroform ...	13·04	Acetylene tetrabromide	− 15·64
Ethyl bromide ...	17·44	Methylene iodide ...	− 26·46
Oleic acid ...	24·62		
Undecyclic acid	32·04		
Dimethylketone	42·37		
Acetic acid ...	45·20		
Ethyl alcohol ...	50·40		

In spreading the drop does not extend as a homogeneous oil phase in the form of a thin lamina but takes place by a process of superficial solution of the oil in a thin film (Hardy's primary layer) which we shall note is unimolecular in thickness; consideration of the mechanism of such spreading will be deferred to a subsequent section. If the area of the water on which the drop is placed is limited in extent the oil continues to spread until the rate of superficial solution is balanced by the rate of return of molecules from the surface film into the lens. The oil of the lens may be regarded

as possessing a definite two-dimensional solubility and equilibrium is attained when

$$\sigma_1 + \sigma_{12} = \sigma_{\text{oily water}}.$$

The surface "pressure" exerted by the film is as we have noted according to Traube and Langmuir defined by

$$F = \sigma_2 - \sigma_{\text{oily water}},$$

whence we obtain for the conditions of equilibrium

$$\sigma_1 + \sigma_{12} - \sigma_2 = -F,$$

or F the "pressure" exerted by the film in equilibrium with the drop is a direct measure of the spreading coefficient*.

This view of the process of spreading and the conditions of equilibrium possesses certain advantages because many solids such as the fatty esters and higher fatty acids spread upon water and their spreading coefficients can only be determined by a direct measure of the film pressure which exists when equilibrium is attained.

Further investigation has shown that the spreading coefficient varies with the temperature, a point which we shall refer to later (p. 87).

In the following table are given a few spreading coefficients for solid materials on a water surface at the melting point determined by Cary (*Proc. Roy. Soc.* A, CIX. 318, 1925) by the above method.

Substance	Melting point °K.	Equilibrium film pressure in dynes per cm.	$\frac{dF}{dT}$ for solid crystal in dynes per cm. per °C.
Undecyclic acid ...	298	38·2	0·588
Lauric acid ...	318	35·1	0·548
Myristic acid ...	327	30·7	0·568
Pentadecyclic acid	325	32·6	0·552
Palmitic acid ...	336	32·1	0·554
Stearic acid ...	344	29·9	0·553
Oleic acid ...	280	30·5	0·517
Hexadecyl acetate	294	34·4	0·637
Octadecyl acetate	305	30·7	0·667
Ethyl palmitate ...	300	19·4	0·669

Spreading of volatile substances on liquid surfaces.

We have noted that a non-volatile substance will spread over a liquid surface or at a liquid-liquid interface by a process of surface

* A small correction is to be made for lenses of finite thickness, see p. 96.

solution in what is primarily a unimolecular film, provided that the magnitudes of the surface tensions of the three interfaces involved are such that

$$\sigma_2 > \sigma_1 + \sigma_{12}.$$

If the substance spreading be volatile it may vaporise from the surface of the liquid and condense on the clean surface of the liquid. As we have noted adsorption of vapour by a liquid surface is *accompanied by a decrease in the free energy of the surface, and* accordingly the vapour will condense on the surface of the liquid to form firstly a unimolecular layer and subsequently a secondary film, if the adsorptive forces be strong enough and the vapour pressure of the spreading liquid be not too low. This type of spreading through the vapour phase may occur even if surface spreading cannot take place. Carbon disulphide will spread on water by this means although surface spreading cannot occur.

2. The unimolecular character of surface films.

If a spreading oil be dissolved in a volatile solvent such as benzene and a definite quantity be placed upon clean water in a dish provided with a movable barrier on the surface so that the area covered by the oil can be contracted or expanded at will, a ready means of varying the surface concentration of the oil thus uniformly spread is provided. Experiments commenced by Miss Pockels and continued by Lord Rayleigh indicated that such an oil film continued to exert the same tension down to a thickness, calculated from the area covered and the quantity of oil put on, of about 50 Å. In the neighbourhood of 16 Å. the tension was rapidly increasing as the film grew thinner until at 10 Å. it did not differ perceptibly from that of pure water. This distance was known to be of the same order as the diameter of a molecule, and Rayleigh suggested therefore that the thinnest oil films possibly consisted of only a single layer of molecules.

Experiments on similar lines were carried out by Devaux (*Ann. Report Smithsonian Inst.*, 1913, p. 261), Marcelin (*J. de Physique*, I. 19, 1914) and Labrouste (*Ann. de Phys.* XIV. 164, 1920). Meanwhile advances in other branches of molecular physics had led to very much more certain values for molecular dimensions, and for triolein. Devaux estimated the thickness of the thinnest film at 10 Å. The

mean molecular distance calculated from the molecular volume and from Perrin's value for the Avogadro number was 11·3 Å., and Devaux concluded that this film was in fact only one molecule thick.

It should be noted that his conclusion is based upon the assumption that the density of the oil in such films is the same as that of oil in bulk. If this were not the case, but if an oil film, for example, had only half the density of ordinary oil, the value calculated for the thickness would be doubled, and we should either have to abandon the unimolecular theory or make the further assumption that the change of density occurred entirely in the direction perpendicular to the surface. This question has hardly been rigorously decided, but the mass of evidence now available strongly supports the unimolecular character of insoluble films upon water. Another assumption tacitly made is that the molecule is approximately symmetrical.

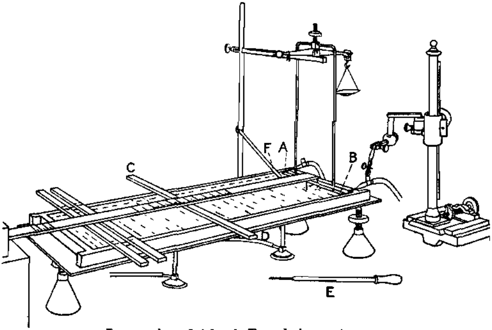
Devaux also advanced the important theory that the characteristics of the solid, liquid and gaseous states of matter are retained so long as one continuous layer of molecules remains unbroken. This conception has been partially confirmed by the work shortly to be described. A film may be solid, liquid, "expanded" or gaseous, and one kind is readily distinguished from another. In certain properties, a solid film of unimolecular thickness resembles quantitatively a three-dimensional solid mass of the same substance, but these properties are necessarily limited to such as can be measured in any given direction.

The compressibility of fatty acid films parallel to the surface appears to be the same as for the material in bulk, but the melting-point, which is not a vectorial property, is very different. If the refractive index of a film could be measured, we should expect to find that in the plane of the surface it was the same as for an extended body of the substance, but different in the perpendicular direction. A solid film in two dimensions, although so closely analogous to its three-dimensional equivalent, must therefore be regarded as a distinct phase.

The effect of temperature upon the properties of thin films was investigated by Labrouste. Below a certain temperature the area of a continuous film of oil remains constant. It then begins to rise

until the area again becomes practically constant at a higher value. The range of temperature within which this change occurs was about 15°. At the lower steady value the film behaved like a rigid solid, so that particles of talc floating on it could not be blown about; at the upper value, on the other hand, floating particles were completely mobile. Labrouste, in fact, observed a somewhat indefinite two-dimensional fusion or volatilisation.

In 1916 Langmuir published his well-known paper on "The fundamental properties of liquids," in which he accepted the conclusion that films of oils on water were unimolecular and made further experiments on the subject by a direct method. Pockels and Rayleigh had measured the surface tension of their films by determining the force necessary to break them, a method open to some obvious objections. The French investigators did not as a rule measure the tensions of the films at all but determined their



Langmuir and Adam's Trough Apparatus.

maximum extension by scattering talc on the surface to make its boundaries visible and observing the maximum area which the film could be made to cover. Langmuir devised a *differential* apparatus which recorded simultaneously the area and the tension of his films. A trough was filled with water. From one arm of a balance was suspended a light horizontal strip of paraffined paper very nearly

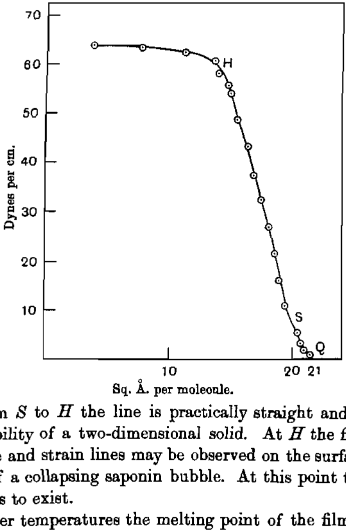
as wide as the trough and just touching its surface. This paper acted as a barrier for the oil film. At the narrow spaces between the barrier and the trough a jet of air played with sufficient force to prevent leakage of oil but not to disturb the barrier sensibly. The trough was provided also with other barriers of paper which could be moved along the trough, pushing before them the film of oil or any impurity. To carry out an experiment the space on one side of the floating barrier was swept clear of impurity, leaving pure water, while on the other side was formed a layer of oil of known volume and of an area controlled by the paper barriers. While the area of the oiled surface was altered the position of the hanging barrier was kept constant by adjusting the weights in the opposite balance-pan. What was measured, therefore, was the difference between the surface tension of pure and of contaminated water. This measurement has the advantage of being direct, involving no rupture or change of condition of the film; further, except under conditions described by Labrouste, it is nearly independent of temperature, whereas the individual tensions of the oily surface, and of pure water, diminish considerably with rise of temperature. Careful temperature control is thus of minor importance.

The quantity of oil was measured, as in previous investigations, by dropping a known volume of a very dilute solution in benzene on the surface, and allowing the solvent to evaporate. Taking Millikan's value, $6{\cdot}06 \times 10^{23}$, for the Avogadro constant Langmuir calculated the number of molecules in his film, and hence the area occupied by each on the assumption of a unimolecular layer: this area he plotted against the *differential tension* which as we have noted is to be regarded rather as a (two-dimensional) pressure exerted on the film and keeping it from spreading out indefinitely.

As an example we shall take the case of palmitic acid on water at 16° C. The figure on p. 70, from Langmuir's paper, shows the compressive force (i.e. the difference, in dynes per cm., between the surface tension of pure water and of the oiled surface) as against the area occupied by one molecule, measured in Ångström units.

At the lowest measurable compression (point Q) the molecular area is 21·8 Å. and the film is perfectly mobile, allowing floating particles of dust to move about freely. As compression is applied

by the moving barrier the area falls, following the curved line *QS*. The lowest part of this line appeared to be asymptotic to the axis of area. At *S* dust particles on the surface lost their mobility as if now held rigidly in position: *S* is thus the melting point of the



film. From *S* to *H* the line is practically straight and gives the compressibility of a two-dimensional solid. At *H* the film begins to crumple and strain lines may be observed on the surface similar to those of a collapsing saponin bubble. At this point the film as such ceases to exist.

At higher temperatures the melting point of the film occurs at higher compressions, like ordinary solids which melt with an increase of volume.

The melting point of the film does not normally coincide, as in this example, with the point at which the line becomes curved. The beginning of curvature of the line may be regarded as corresponding to a process of two-dimensional evaporation, for if the straight parts of the curve resemble the compression curves of solids and liquids, the curved portions resemble those for a gas near its critical point.

We have seen that earlier experimenters on the subject of thin films had reached the conclusion that these films were probably only one molecule in thickness. Rayleigh had suggested, that at the point corresponding to Q (Fig. p. 70), where the oil first exercises an appreciable effect on the surface tension of water, the film was one molecule thick, but that at the point H, where the maximum effect on the surface tension is reached, the film becomes bimolecular. Marcelin supported the theory of Rayleigh on the grounds of his own experiments with oleic acid, in which the quantity of oil required to cover the surface at the minimum surface tension H was one-half that necessary at the maximum tension Q. Devaux however pointed out that the ratio was not so great as two to one in any case, and explained the phenomenon by supposing the molecules to be capable of looser or tighter packing.

The theories offered so far gave no clue to the origin of the unimolecular films. Langmuir however pointed out that if the molecules in the film are regularly orientated on the surface of the water owing to the attraction between the water and the active groups of the organic liquid, these groups e.g. —COOH —CH_2OH, are dissolved as it were in water. The long hydrocarbon chains attached to them have no tendency to dissolve and stand up vertically over the surface. "It is therefore evident," says Langmuir, "that there should be no particular reason for another layer of oil molecules to spread out on top of the first to form a second layer. In fact since this upper portion consists exclusively of CH_3 (or C_2H_5) groups, while in a globule of oleic acid, carboxyl groups are distributed through the mass, it is natural that the oil should prefer to remain in globule, rather than spread out as a layer two molecules deep. In the mass of liquid the carboxyl groups probably tend to gather into clusters, because of the greater affinity of these groups for one another than for the hydrocarbon chains."

3. Molecular Size.

Using the method of Devaux, Langmuir determined the maximum area (point Q) for a molecule of various substances all of which possess an "active group," such as —CO_2H or —CH_2OH, together with a long hydrocarbon chain. His results are given in the table.

The lengths of molecules are obtained by dividing the cross-section into the volume per molecule calculated from the molecular volume and Millikan's value $6{\cdot}06 \times 10^{23}$, for the Avogadro number.

Substance	No. of C atoms	Cross-section Å.	$\sqrt{\text{Cross-section}}$ Å.	Length Å.	Length per C atom Å.
Palmitic acid ...	16	21	4·6	24·0	1·5
Stearic acid ...	18	22	4·7	25·0	1·39
Cerotic acid ...	26	25	5·0	31·0	1·20
Tristearin ...	57	66	8·1	25·0	1·32
Oleic acid ...	18	46	6·8	11·2	0·62
Triolein	57	126	11·2	13·0	0·69
Trielaidin ...	57	120	11·0	13·6	0·72
Myricyl alcohol ...	31	27	5·2	41·0	1·37

The table shows that many molecules are far from being symmetrical in shape, a direct confirmation of his theory. We notice incidentally the need for care in calculating the number of molecular layers contained in a thin film by the method of Rayleigh and Devaux, without further consideration. (If for example Devaux had chosen cerotic acid instead of triolein as his test case, he would have found 31 Å. as the thickness of the film, whereas the cube root of the volume of a molecule is $\sqrt[3]{31 \times 25} = 9{\cdot}2$ Å. Thus, neglecting the shape of the molecule, cerotic acid would have appeared to form a trimolecular layer.)

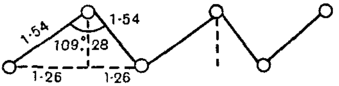
The cross-sections of the saturated acids do not vary much, but the length increases with the number of atoms in the carbon chain, as would be expected from Langmuir's theory. The alcohol has a somewhat greater cross-section than the acids. The cross-section of the glycerides is about three times as great as that of the acids from which they are derived, a fact easily explained on the supposition that the three acidic chains in each case lie side by side, occupying as much area on the water as if they were in separate acid molecules.

The case of oleic acid, which, with the same number of carbon atoms as stearic acid, occupies double the area on water, was explained by Langmuir on the grounds that the water dissolves not only the carboxyl group but also the ethylenic linkage, so

that the molecule is doubled back upon itself. In view of later work this explanation is a little doubtful.

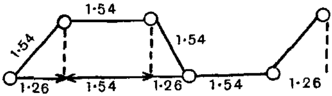
The length per carbon atom (after allowing for the occurrence of parallel chains) gives the average vertical distance between these atoms. It is striking that these distances are considerably less than that found by X-ray analysis for the distance between adjacent carbon atoms in a diamond, namely 1·5 Å. We should expect this figure to represent roughly the minimum distance to which two carbon atoms are capable of approaching, and it may be inferred that the carbon atoms in the long chain compounds do not lie vertically one over the next, but form a spiral column.

Confirmation of this hypothesis is obtained by the X-ray examination of soaps and fatty esters by Shearer, Piper, Grindley and Müller (*J.C.S.* CXXIII. 2043, 1923) (see also Friedrich, *Physikal. Zeit.* XIV. 317, 1913, De Broglie, *C.R.* CLXXVI. 738, 1923, Becker and Jahnke, *Z. Phys. Chem.* XCIX. 242, 1923), who have shown that two types of chain formation occur in carbon compounds in accordance with our preconceived views on the tetrahedral orientation of the valencies of the carbon atom. The spacing of the planes in these two types is indicated in the following diagram:



Chain.

$$\text{Mean } d = \frac{2{\cdot}52}{2} = 1{\cdot}26 \text{ Å}.$$



Carboxyl.

$$\text{Mean } d = \frac{2{\cdot}80}{2} = 1{\cdot}40 \text{ Å}.$$

Langmuir's "orientation" theory, providing as it does both a numerical confirmation and an explanation of the occurrence of unimolecular layers is capable of wide application. Oriented molecular layers in all probability govern the behaviour under friction of thinly lubricated solid surfaces: efficient lubricants are similar in chemical character to those substances which form stable thin films upon water. The force which attaches the carboxyl or other "active" group of the long chain compound to the water is of the same kind as that holding to a metallic nucleus of copper, cobalt or platinum, the ammonia or amine in a so-called coordinated compound. The upper part of a molecule in a thin film of palmitic acid on water has the properties of a hydrocarbon, just as the more complex homologues of the ammonio-cupric salts, such as the higher amino-acid derivatives, retain all the properties of those parts of the molecule which are remote from the copper nucleus. The difference between an ordinary compound, a coordination compound and an adsorption compound is one of degree and not of kind: the same pair of atomic groups may combine under different circumstances to form any of these types of compounds. We cannot make any distinction between physical and chemical forces, but should rather try to discover what causes strengthen or weaken the atomic attraction.

The behaviour of the higher fatty acids in thin films may well be compared with that of the smectic or string-like anisotropic crystalline liquids: these liquids consist of molecules of the long chain type and exhibit the property of orientation. They differ in containing groups of oriented molecules in three dimensions instead of two, and this difference is probably to be accounted for by the properties of the parts of their molecules remote from the active group. A great lateral attraction, due perhaps to the greater length of the carbon chain, may allow molecules to be attached in parallel but in échelon; added to which, the existence of more than one active group may allow an end-to-end arrangement to be built up.

The orientation theory has made possible a great advance in our knowledge of molecular architecture, and Langmuir's work on this subject has been continued with great success by Adam. The experimental method was unchanged except for the substitution

of a brass for a porcelain vessel, glass movable barriers in place of paper and a light vertical hanging barrier for a horizontal one.

In the curve for a "condensed" film of palmitic acid (viz. one on which the molecules appear to be in direct contact, i.e. solid or liquid), the compressibility line is divided into two parts of which the upper is by far the steeper. The steep part of the curve is reproduced in the cases of a large number of other acids and of their derivatives. If produced down it meets the axis of area at the point $A = 20{\cdot}7$ Å. The lower section of the curve meets the axis, in the case of palmitic and the other saturated acids, at $A = 25{\cdot}1$ Å., but this coordinate depends on the character of the active group and may be greater or less. Thus for cetyl alcohol it is 21·7, for octadecyl urea 26·3. The quantity $A = 20{\cdot}7$ Å. found for the intersection of the steeper line with the axis of area is characteristic of all the hydrocarbon derivatives considered. Chemically their similarity depends on their common structure as a chain of CH_2 groups. Adam therefore suggested that the area 20·7 Å. was the effective cross-section of the CH_2 chain: the suggestion is supported by the very fair agreement with the value, 19·3 Å., calculated for the surface of a $—CH_2$ group, taking 17·8 c.c.s as the molecular volume of the group, and 1·52 Å. or the distance between carbon atoms in a diamond, as its length.

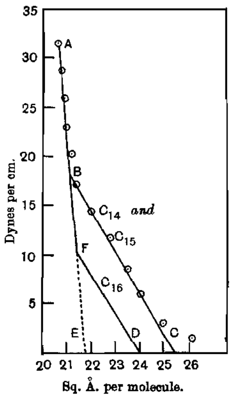
Even more satisfactory is the agreement between the calculated and observed values for the cross-section of aromatic heads. From the table on p. 77, the cross-section of the group $—C_6H_4OH$ is 23·8 Å. and of $—C_6H_4.NH_2$ 23·71 Å. Since the polar groups OH or NH_2 must orient themselves towards the water and the hydrocarbon chain away from it, the cross-section actually measured is probably that of the benzene nucleus itself, although the possibility of a tilting effect has to be borne in mind*. Now from X-ray measurements by Shearer the effective cross-section of a benzene molecule itself in a crystal of benzene is 23·3 Å. Again, from Adam's measurements, the compressibility of aromatic heads gives a decrease of 1 per cent. in area for an additional compressive

* It will be noted that the limiting area of a phenol molecule on the surface of water and salt solutions was likewise found to be 23·8 Å. in Ch. II.

force of 5·8 dynes per centimetre. If the resistance of the film to compression is provided by the benzene nuclei which have a thickness of approximately 6 Å., this force is equivalent to 97 × 10^6 dynes per square centimetre. The force required to diminish the volume of liquid benzene by 1 per cent. is 113 × 10^6 dynes per sq. cm. at ordinary temperatures.

The more gently sloping lines correspond to a state of expansion in which the mean cross-section is governed by the characteristic active group, and the curves naturally differ according to the nature of this group.

Adam's results for three of the higher normal aldoximes are reproduced in the curve. The line *AB*, common to all three, closely resembles the usual line giving the compressibility of the hydrocarbon chains, though the somewhat greater value for the area, 21·8 Å., at which it cuts the axis of area, may be due to some other form of packing. The lower part of the line has different though parallel courses for the compound with 16 carbon atoms and for those with 14 or 15: the lines *BC* and *FD* represent the more open type of packing which is determined by the area of the head, or soluble end, of the molecule. The area of the head when unconstrained is thus 25·4 Å. for the lower and 24·0 Å. for the higher homologue. The compressibility of the film, expressed by the slope of these lines, is the same in both cases. This may not be actually the compressibility of the head-groups themselves, but, as Peters suggests, the heads may be forced by compression to leave their original alignment in the plane of the water, and move up or down into positions in échelon.



The following table gives the values obtained for the head groups so far investigated :

Head group	Area in sq. Å.	Notes
—COOH	25·1	
—$COOCH_3$	22·3	
$COOC_2H_5$	22·3	
$COOCH_2CH=CH_2$	22·3	
$CONH_2$	21·0	
$CONH\phi$	25·8	Above 29° C.
	28·2	Below 24° C.
CHBrCOOH ...	27·2	This group can pack in two
	32·8	ways.
—CN	27·5	
CH=CHCOOH ...	28·7	
$CH=CHCOOC_2H_5$	28·7	
—NC	27·5	
C=NOH	24·0	
	25·4	
CH_2OH	21·6	
CH_2OCOCH_3 ...	23·0	
$NHCONH_2$	24·8	
	26·3	
$C_6H_4NHCOCH_3$ ...	28·2	Two-dimensional allotropes.
	25·8	
—$C_6H_4 . NH_2$ ...	23·7	
—C_6H_4OH	23·8	
—$C_6H_4OCH_3$ ...	23·8	
Hydrocarbon chain	20·7	
Triglycerides ...	63·0	
Glycol dipalmitate	42·0	
Cholesterol	39·0	
Hydrolecithin ...	53·0	

The slope of the line *AB* for fatty acids shows a decrease in area of about 0·8 per cent. for an increase of 10 dynes per centimetre: for chains of 18 carbon atoms or over, values as low as 0·4 per cent. have been found. If we take the latter value, and calculate the surface compressibility of palmitic acid on the assumption that the length of the molecule is 21·1 Å., we find that a force of *119 megabars is required for a contraction of 1* per cent. The volume compressibility of the paraffin $C_{15}H_{32}$ is given as 125 megabars for the same contraction, and the agreement found is fully as good as could be expected.

Most films are solid in the region S′H, but cetyl alcohol is an exception, and supercooling is sometimes observed in other cases. On the other hand, with the exception of the substituted ureas, films are not solid when the heads alone are closely packed.

The substituted acetamides

$$C_{16}H_{33}NHCOCH_3 \text{ and } C_{17}H_{35}NHCOCH_3$$

melt, with increase of area at a definite temperature, depending on the pressure. At 1·44 dynes per cm. the melting points are 9° and 17° C. respectively, and increase of compression, as we should expect, raises the melting point.

A somewhat similar phenomenon is observed with substituted ureas, which also have two condensed films stable at the same pressure but within different temperature ranges. Here rise of temperature at the transition point produces a diminution of area, and pressure lowers the transition point.

Remarkable results were obtained with pentaerythritol tetrapalmitate. This symmetrical body gave a film of exceptional rigidity, so that it withstood a force at one end of 5·6 dynes per cm. without any support at the other end. When first put on the area was 100 Å. per molecule and was reducible by compression to 80 Å., or about four times the area of a single closely packed chain. The four chains must therefore lie parallel, and two of them must be bent back through a large angle.

4. Collapse of condensed films.

The compression under which collapse of the films occurs is very variable. In the case of palmitic acid the buckling point occurred between 20 and 45 dynes per centimetre, when the experiments were carried out with fresh water. On the other hand when water with a P_H of about 6 was used, the film, after being allowed to stand for a few days either covered or open to the atmosphere, resisted compression to over 60 dynes per centimetre.

The effect of the collapse of a film is to make the surface visible by local thickening where groups of molecules have been ejected under the strain: it was observed by Labrouste and Adam that where the film was liquid the ejected molecules returned to form an integral part of the film as soon as the strain was removed, whereas with solid films they retain their ejected position and hence their visibility. Solid films appear to be ejected in a definitely crystalline form. The groups of crystals so formed radiate from central nuclei. They may be broken up by disturbance

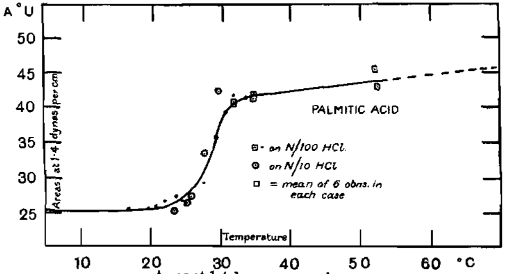
with an air-jet, but as soon as blowing is discontinued the crystal groups reform very rapidly.

It is possible that solid ejected films would return to the surface phase if sufficient time were permitted to re-establish equilibrium. On the other hand the polar groups which have been removed forcibly from the water surface may be heavily solvated and the structure of the ejected material may approximate to that of a partly crystallised soap film possessing but little tendency towards adhesion with a water surface.

5. Expanded Films.

Labrouste was the first to notice that below a definite temperature the area of a continuous film of oil remained constant, the area commencing to increase above this temperature until it becomes practically constant at a higher value. This change in area took place over a temperature range of about 18°. This phenomenon has been investigated in detail by Adam who has assigned the name of "expanded film" to the superficial phase in this state.

Adam has measured the increase in area necessary on elevation of the temperature under conditions of constant compression. A typical A, T curve under a pressure of 1·4 dynes per cm. is shown in the following diagram.



Areas at 1·4 dynes compression.

It will be noted that the existence of a temperature range of expansion *ca.* 13° C. is confirmed, the temperature of half expansion

being in this case 28·5° C., whilst the area of the expanded film at this F value is *ca.* 41 Å. Langmuir in his investigations on the areas occupied by fatty acid molecules on the surface of water obtained an area of 46 Å. for oleic acid as compared with 21–25 Å. for the saturated fatty acids and imagined that the double bond in the unsaturated acid bent down to make contact with the water. In reality as Adam showed this is not the case, for oleic acid, at the temperatures at which Langmuir's investigations were carried out, forms an expanded film in which the area occupied is about twice that of the same acid in the condensed state.

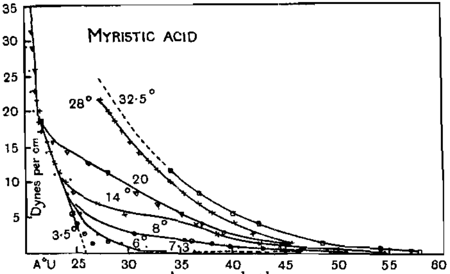
The expansion temperature ranges for a number of acids at 1·4 dynes per cm. compression have been obtained by Adam with the following results.

Substance	Temperature of half expansion	Area of expanded film corrected to 0° C. in Å. (on assumption of gaseous expansion)
Palmitic acid	28·5	36·8
Methyl palmitate	27·5	46
Ethyl "	13	55
Propyl "	< 5	76
n-Butyl "	< 5	74
n-Octyl "	< 5	76
Ethyl stearate	33	45·4
Tripalmitin	48	29·5
Tristearin	57	29·9
Cetyl alcohol	49	30·8
Heptadecylurea	55	33
Stearic amide	58	32·2
Stearic nitrile	26	36·4
Octadecylamine hydrochloride	26·5	46
Stearic acid	46	36·1
Oleic acid	< 0	50·5
Lauric acid	< 0	45·1
Tridecyclic acid...	< 0	42·5
Myristic acid.	9	40·6
Pentadecyclic acid	19·5	38·8
Margaric acid	37·5	36·6

It will be noted that the expansion temperature for an acid increases with the length of the hydrocarbon chain (about 8° C. per CH_2), there being no difference between the odd and even numbers of the series as exists in the melting points of the crystals

whilst there is a progressive decrease in the apparent expansion area at 1·4 dynes compression for the acids as the chain increases.

Adam has likewise examined the *F*, *A* curves for a substance such as myristic acid (temperature of half expansion under 1·4 dynes per cm. 9°) over both the region of condensed and that of expanded film. A few of the isotherms obtained for myristic acid are given in the diagram.



Area per molecule.

The temperature at which expansion commences is defined by the pressure to which the film is exposed and above a certain critical temperature it is probable that the existence of a condensed film is impossible.

The apparent similarity of the *F*, *A* curves of myristic acid to the *P*, *V* curves for an easily liquefiable gas such as carbon dioxide has led Adam to suggest that the molecules in the expanded films of these substances are in a similar state to those of say carbon dioxide in the vapour state. He adduces as further argument in support of this hypothesis, the much greater coefficient of compression of expanded films. Again it is evident that the molecules are not lying down flat in the expanded state, for the increased area even under low compressions is only 50 Å., whilst for stearic acid of lengtb 21 Å. and of cross-section 5·2 Å. a horizontal molecule would occupy at least 109 Å. of area; at the same time the area per molecule decreases somewhat as the length of the hydrocarbon chain increases.

There are however somewhat cogent objections to the supposition that "expanded films" are identical in properties with the "gas" films which are formed from the solutions of the lower fatty acids (see Ch. II). In the first case the important observation that an expanded film occupies a definite area and is incapable of continuous expansion on decrease of the pressure can be noted by placing a small drop of oleic acid on a large water surface. The spreading to an expanded film of definite area occurs. Again Cary has shown that if a definite area of fully expanded film be taken and a small increase in the water area available be made, the surface tension will be that of pure water within a few tenths of a dyne per cm. The true "vapour pressure" of an expanded film is thus very small*. In an attempt to apply an equation applicable to gas films, viz. $F(A - B) = xRT$, to expanded films, it is found that distinct irregularities in the curves are obtained, furthermore the values of x for expanded films of myristic acid are extremely small. This can be interpreted on the hypothesis that the lateral molecular adhesion is very large, so large in fact for long chain compounds that practically every collision between the orientated molecules on the surface is an inelastic collision.

On this view expanded films must be regarded as a network of hydrocarbon chains adhering to one another with their lower polar heads occupying a relatively large area on the water surface and being in violent thermal agitation. Evidently two such molecules adhering to one another by their chains will spread out on the surface, the molecules being inclined to one another. They will never lie flat on the surface except possibly at the moment when a vigorous lateral agitation separates one molecule from another. As the chain length increases the lateral adhesion increases and the area occupied by the two molecules decreases, as experimentally noted.

6. The mechanism of spreading of non-volatile substances on liquid surfaces.

An examination of the mechanism of spreading of solids on water has indicated that the process takes place in somewhat the following manner. At a certain critical temperature the magni-

* Adam (*Proc. Roy. Soc.* cx. 423, 1926) has recently obtained the following values for the vapour pressures. Myristic acid 0·20 dynes per cm. Palmitic acid 0·04 dynes per cm. Ethyl stearate 0·025 dynes per cm.

tudes of the spreading coefficient and of the kinetic energy of the molecule have risen (together) to such a value that a molecule can be torn off from the crystal surface* exposed to the water. The molecules thus detached exert a "vapour pressure" which gradually rises until it reaches the critical value for the formation of an expanded film. As a result of such surface solution an expanded film (see p. 79) grows round the crystal surface at a definite rate. The rate of solution at any temperature is constant for a definite area of interface of a given material and the expanded film is gradually compressed. For slow rates of solution the surface tension of the water is hardly affected at all until the whole area of the surface is covered with such an expanded film. Further the rate of solution is slow enough to push out the film already formed without any sensible pressure gradient occurring in the film from crystal to edge. In cases of liquid acids however, e.g. oleic acid, the rate of surface solution is so rapid at ordinary temperatures that the expanded film formed round the lens is pushed out with great speed. At these high speeds there is a hy no means inconsiderahle resistance to the motion of the expanding disc of expanded film and a surface pressure, i.e. a fall in surface tension amounting in the case of oleic acid to several dynes per cm., may be observed in the neighbourhood of a lens surrounded by the expanded film which is being formed by such surface solution. On a limited area of water the surface tension commences to be lowered when the further surface solution of the crystal commences to compress the expanded film. Compression by surface solution continues until the equilibrium value F is reached.

An examination of the rate of such compression for expanded films reveals the fact that they obey a law of the type

$$\frac{dF}{dt} = k(F_0 - F),$$

where F_0 is the saturation value.

It may readily be imagined that the equilibrium finally attained is a dynamic one in which the rate of solution

$$\frac{dn}{dt} = k'$$

* It is somewhat remarkable that surface solution only occurs at the edge of the crystal exposed to water-air interface and solution does not occur from the parts of the crystal immersed in the water.

is balanced by the rate of return of molecules to the surface, or

$$\frac{dn'}{dt} = kF_0 \quad \text{or} \quad \frac{k'}{k} = F_0,$$

at a rate proportional to the surface pressure.

Hence the rate of compression will be defined by the equation

$$\frac{dn}{dt} - \frac{dn'}{dt} = k' - kF = \frac{dF}{dt},$$

whence
$$\frac{dF}{dt} = k\left\{\frac{k'}{k} - F\right\} = k\{F_0 - F\}$$

in agreement with the results obtained by Cary.

A few of the experimental data are given below.

Influence of temperature on time required to cover an area of 56·9 *sq. cm. of water with a unimolecular film under zero compression of myristic acid. Length of water acid interface* 0·251 *cm.*

Temperature °K.	Time in minutes
288	>12
293	6·8
298	2·2
303	0·7
308	0·3
313	0·2

Rate of saturation of a surface of N/100 HCl *by solid myristic acid. Area of surface* 56·9 *sq. cm. Length of crystal water interface* 0·251 *cm.* $T = 25°$ C.

F dynes per cm.	t calc.	t obs.
0	—	2·05
3·22	2·81	2·85
6·44	3·95	4·00
9·66	6·50	6·80
10·31	7·76	8·10

If the film formed by superficial solution is an expanded film a low pressures but condensed at high pressures, it is found that th unimolecular character of the compression time curve is obeyed

until a critical value of F is reached at which the expanded film no longer undergoes gradual compression but is converted into a condensed film. The surface pressure accordingly increases much more slowly with the time than it would if such a transformation to a material of smaller molecular area were not occurring. This is well exemplified in the rate of compression of films of myristic acid at 25° C. and at 18° C. At the higher temperature the film is always expanded up to the equilibrium value of F. At 18° C. conversion from an expanded film to a condensed film occurs at a pressure of five dynes per cm. It is important to note that the film spreading from the crystal is not being pulled out by a differential tension between the edge of the film and the water but is being pushed out by the solution of molecules at the crystal surface.

If the expansion rate be very rapid we notice that the layer spreading out from the drop is frequently of multimolecular thickness as noted by the formation of interference colours. After a few seconds however (usually from two to three), the excess oil above that necessary to form a unimolecular thickness is pulled back into the lens or more generally into a number of minute lenses formed from nuclei resulting from dispersion of the original drop. This phenomenon noted by Devaux does not appear to occur when pure oils are employed, but may readily be observed if a small quantity of benzene be added to the oil.

Since the rate of solution of the crystal is constant the rate of increase of area of the expanded film varies inversely as the radius of the circular film. If the spreading be determined in a narrow trough where the expanding area touches the side of the trough the film would, if rigid, undergo compression in this direction and continue to expand at the normal rate over the other portion of the full surface. Actually the film is not rigid and an augmentation in the velocity of spread in the "wave" front is noted. Thus, if a drop of oleic acid be placed on water in a circular trough in a position half-way along the radius from the centre it will be observed that the "wave" front, at first circular, begins to move with increasing velocity at the point where it comes in contact with the trough rim and the two horns travelling round each side of the trough edge will arrive at the point on the continuation of

the radius at the far end of the trough in the same time as the direct portion moving there by expansion.

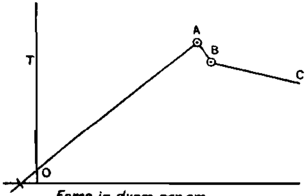
7. The spreading of mixtures.

Very few experiments have been made on the spreading of mixtures. One or two observations of some interest may however be made in this connection. If a small quantity of a slow spreading material be dissolved in one that spreads rapidly and the mixture be placed on a water surface, a unimolecular equilibrium layer of the second is rapidly formed. In the course of time the slow spreading material arrives at the oil-water interface and if the magnitude of σ_{AB} for the second oil be less than that of the first, the lens may actually spread out into a thin sheet. Again, if two crystals of fatty acids be placed upon a limited area of water, the equilibrium pressure will be found to be that of the fatty acid of higher surface pressure. In the case of two lenses of liquid fatty acid the equilibrium surface pressure may actually be higher than that of either acid in the pure state. It is possible that the formation of solid solutions as well as of liquids of higher surface solubility than the pure substances might be revealed by careful examination of such systems.

8. The heats of transformation of surface phases.

In discussing the conditions of spreading of insoluble oils on the surface of water, we noted that either a liquid lens or a solid crystal of a spreading but insoluble and non-volatile substance when placed upon the surface of water would continue to spread, in the form of a unimolecular film, until at any definite temperature the surface tension of the water had fallen to a characteristic value for the substance; the lowering of the surface tension thus produced $\sigma_0 - \sigma = F$ might be regarded as a measure of the surface solubility of the solid or liquid under investigation (similar to the osmotic pressure in the case of bulk solution). The surface phase may however be either gaseous, solid, liquid or expanded and the equilibrium pressure will likewise vary if the bulk phase be solid or liquid. Cary (*Proc. Roy. Soc.* A, CIX. 318, 1925) has determined in the writer's laboratory the variation in the equilibrium pressure with the temperature for a number of solid and liquid organic insoluble

substances by the ring method. As typical may be given the following curve for stearic acid.



It is found that no perceptible (to 0·5 dyne per cm.) lowering of the surface tension of the water occurs until the temperature reaches a well defined value *O*. A few of these limiting temperatures are given in the following table:

Compound	Temperature of commencement of surface solution °K.
C_{11} chain acid ...	233
C_{12} " " ...	254
C_{14} " " ...	273
C_{15} " " ...	266
C_{16} " " ...	278
C_{18} " " ...	290
Oleic acid	221
Hexadecyl acetate ...	240
Octadecyl acetate ...	259
Ethyl palmitate ...	271

We must imagine that some of the molecules in the crystalline solid have carboxyl groups wetted by the water on the line of contact, these groups although attached to the water cannot pull off the hydrocarbon chain at low temperatures. At 17° C., however, in the case of stearic acid the force of dissolution and the kinetic energy of the molecule are sufficient to permit of rupture. The molecule now floats freely on the surface of the water. During the course of time a number of molecules are so detached, they do not however exert any appreciable action on the tension of the water

since every collision between free molecules is inelastic. In this manner a film of molecules upon the surface of the water then commences to pack and lower the surface tension. The point O (Fig. p. 87) may be considered as the equilibrium point of the system solid crystal, film, water.

From the point of view of the phase rule

$$P + F = C + 2,$$

we may regard the system as one component consisting of fatty acid, or as a two-component system fatty acid and water. In the latter case there is an additional restraint on the system in accordance with the expression

$$\Gamma_1 d\mu_2 = -\Gamma_2 d\mu_1.$$

At O three phases exist in equilibrium, hence $F = 0$ or O is an invariant point. On elevation of the temperature the water phase disappears and the system becomes divariant. Along the line OA the surface film at first solid is observed to melt. No abrupt melting point can however be noted and no break is observed in the line OA.

At A the crystal melts and there are present three phases: solid crystal, liquid lens and film. The system is accordingly nonvariant.

The F, T curve beyond this point is again linear, but the surface pressure decreases rapidly with elevation of the temperature until the point B is reached where an abrupt change in the slope of the curve is noted. In many cases such as in the long chain esters the film is found to be condensed at A and expanded at B, thus AB is the expansion interval of Labrouste and Adam. For acids on the other hand with the exception of stearic, the film is already expanded at the melting point and the portion of the curve AB is missing.

Since the equilibrium pressure F is a measure of two surface tensions

$$\sigma_{\text{oil}} + \sigma_{\text{interface}}$$

it is clear that in those cases where the portion of the curve AB exists, the interfacial surface tension must change rapidly with the temperature over the portion AB and move slowly over the region BC. In the film these two portions of the curve are associated

with a transition from a condensed to an expanded film and with this analogy we may regard the oil-water interface as being capable of existing in two states, condensed and expanded. At B the oil-water interface is expanded and has the usual small temperature coefficient, at A the interface is condensed or partly expanded and possesses a high temperature coefficient although the interface may not necessarily expand at the same temperature as the film. Thus the interface may be condensed, partly expanded or completely expanded at the melting point, the actual state being determined by the length of the AB curve and the film area at the melting point.

A number of expansion temperatures, i.e. temperatures at B, together with the equilibrium pressures are given in the following table, which can be compared with the data presented on pp. 64, 65.

Compound	Temperature of expansion in ° K.	F. equilibrium pressure in dynes per cm.
Stearic acid	350	26·3
Hexadecyl acetate ...	310	19·6
Octadecyl acetate ...	321	16·0
Ethyl palmitate ...	306	14·3

From the slopes of the various segments of the curves together with a knowledge of the areas of the molecules at the invariant points it is possible to calculate the latent heat of change from the bulk phase to the surface.

Thus in the case of stearic acid the slopes of the curves are

$$OA \qquad \frac{dF}{dT} = +0{\cdot}553 \text{ dyne per cm. per } ^\circ\text{C.}$$

$$AB \qquad \frac{dF}{dT} = -0{\cdot}67 \quad ,, \quad ,,$$

$$BC \qquad \frac{dF}{dT} = -0{\cdot}153 \quad ,, \quad ,,$$

Writing the equations for the conditions of equilibrium of the film with the crystal at B, we obtain

$$d\mu = -S_1 dT + AdF \text{ for the film,}$$

$$d\mu = -S_2 dT + vdP \text{ for the crystal.}$$

Since P is constant $vdP=0$ and by eliminating $d\mu$ we obtain

$$\frac{dF}{dT}=\frac{S_1-S_2}{A}=-\frac{L}{TA},$$

inserting the value $A=24{\cdot}3\times 6{\cdot}06\times 10^{18}$ sq. cm. per gm. mol. we obtain $L=6{,}000$ calories as the superficial latent heat of spreading of the solid acid and $L=-9{,}000$ as the superficial latent heat involved in the spreading of the film from the liquid lens and the expansion of the liquid interface. Together we obtain $L_f=15{,}000$ calories as the latent heat of fusion of stearic acid. From data on the heat of fusion of the acids the areas of the molecules at the melting points may be calculated with the following results:

Normal acid carbon atoms	Area at M.P. in Å.
11	25·3
12	26·8
14	32·1
15	35·2
16	38·0
18	24·3

Thus of the two factors involved in the expansion increase in length of chain and increase in melting point temperature, the latter is more important than the former up to a chain length of C_{18} atoms at which the interface and film are almost condensed again.

9. Spreading on solid surfaces.

In the cases which we have considered in some detail, spreading is occasioned by the movement of a unimolecular layer of molecules across the water surface. Since the polar heads of the molecules are immersed in the water and possibly solvated, some movement of the molecules of the surface layer of the liquid must occur. In the case of solids such motion cannot occur and as demonstrated by Hardy, spreading does not take place. If however a solid surface be just covered with a thin layer of water molecules

spreading of an oil will take place with great ease. We have noted in discussing the adsorption of vapours by liquids that liquid mercury readily adsorbs many vapours and we shall have occasion to note that this adsorptive power is also present at solid surfaces; thus a crystal or lens of a substance may spread over a solid surface by a process of vaporisation from the bulk solid or liquid followed by condensation and adherence on the solid surface (see Hardy, *Report to Solway Conference*, Brussels, 1925).

Soap films.

We have noted that the adhesion of the polar groups to water and to one another is much greater than the weak adhesion of hydrocarbon chains either to water or to one another. It is thus reasonable to assume, an anticipation verified by Perrin (*Ann. Phys.* x. 160, 1918), that soap films may be made up of composite surfaces each of which consists of two layers of orientated molecules of soap the outer surface of each side consisting of hydrocarbon chains and the polar groups held together with water as a sandwich between the orientated hydrocarbon chains. These elementary leaflets which will possess but little adhesion for one another may be built up to form thick films similar in structure to the crystalline fatty acids examined by Shearer (see p. 73). The leaflets may slip over one another with great ease, thus providing the play of interference colours noticed in soap films. The elementary leaflet has in fact been shown by Perrin and others to be two molecules in thickness.

The permeability of soap films has been examined in detail by Dewar who showed (*Proc. R. I.* XXII. 193, 1917) that the rate of penetration varied with both the film thickness and the excess pressure in the bubble. A few of the values obtained for hydrogen are cited overleaf.

Bubbles which are made of glycerine and soap adsorb water when placed over a vessel containing water. The bubble thickens and eventually drops fall off. When the soap glycerine content of the bubble is reduced to one or two per cent. by this process of drainage drop formation ceases, the bubble becomes thin and black and if maintained in a uniform temperature enclosure may be preserved for considerable periods. The rate of condensation of

the water per sq. cm. of bubble surface is found to be inversely proportional to the age of the bubble and to obey the equation

$$\frac{dx}{dt} \cdot t = 0{\cdot}705,$$

where x = milligrammes condensed per sq. cm. and t is the time in days.

BLACK BUBBLE.

Diameter cm.	4	6	8	10
Gas transfer in c.c. per sq. cm. per diem	·22	·14	·10	·053
Internal pressure mm.	·45	·30	·23	·18

GOLDEN YELLOW BUBBLE.

Diameter cm.	4	6	8
Gas transfer in c.c. per sq. cm. per diem	·285	·103	·050
Internal pressure mm.	·55	·103	·050

During this period the concentration of soap and glycerine in the bubble becomes progressively weaker, thus the rate of condensation is proportional to the concentration of the solutes in the soap film.

The rates of evaporation of water through unimolecular films has been examined by Hedestrom and by the writer*. It is found that the rate of evaporation of water through unimolecular films of fatty acids on the surface of water is relatively slow in comparison to the high rate of evaporation calculated with the aid of the Herz-Knudsen equation. The rate is approximately inversely proportional to the surface film pressure F as is indicated from the following figures.

* *Jour. Phys. Chem.* XXIX. 1585, 1925.

Temperature 25° C.		
Acid	F in dynes per cm.	Rate of evaporation in mgm. per sq. cm. per minute
Stearic ...	5	44·9
Lauric ...	26·3	36·0
Oleic ...	29·1	29·7
Theoretical maximum ...	...	17,820

Temperature 35° C.		
Acid	F in dynes per cm.	Rate of evaporation in mgm. per sq. cm. per minute
Stearic ...	9·27	69·9
Lauric ...	28·35	59·7
Oleic ...	28·8	43·9
Theoretical maximum ...	...	26,910

10. Lubrication of surfaces.

The lubrication of metallic and other surfaces has been studied in detail by Hardy. Hardy has shown that surface spreading never occurs on solid surfaces and any spreading that does occur takes place through the vapour phase. Again, although the primary or unimolecular film is adsorbed extremely strongly to metallic surfaces when the substance contains a polar group such as the —COOH or —OH, yet a secondary film consisting of a relatively thick multimolecular layer is generally built up. This secondary film takes a relatively long period of time to adjust itself and it appears probable that molecular orientation is proceeding in the layers of the oil at a rate much slower than for the underlying unimolecular layer. On placing a load on a lubricated surface the load floats on the multimolecular layer which can be squeezed out by increasing the load until presumably a bimolecular layer with the molecules orientated towards the metal and load

interface is left. The friction gradually rises as the multimolecular layer is squeezed out until it acquires a constant value dependent on the chemical constitution of the lubricant. Hardy has shown that the coefficient of friction may be expressed in the following form

$$\mu = b_0 - d - c\,(N - 2),$$

where N is the number of carbon atoms in the chain, b_0 the friction of the chain faces, i.e., is a pure function of the chemical nature of the solid, d is the decrement due to the end groups attached to the chain. When N exceeds fifteen in the fatty acid series μ vanishes and the smallest traction that can be applied produces slip. It is clear that the carbon atoms in the chain provide solely a method of separating the active ends metal/carboxyl from one another and in themselves exert no effect on the lubricating power. We shall have occasion to note that the electric moment of a hydrocarbon chain appears to be vanishingly small when measured by the electrification produced at air-liquid interfaces, a fact which may be of importance in the ultimate analysis of the mechanism of cohesion and friction.

CHAPTER IV

LIQUID-LIQUID INTERFACES

1. Introduction.

There exists as we have noted a separate phase at the interface between a liquid and a gas. The magnitude of the vapour-liquid interfacial energy is markedly dependent on the composition of the liquid and although experimental data are somewhat scanty, the surface energy is also affected by the nature of the gas in contact with it. It is to be anticipated that at the interface between two immiscible liquids a similar new interfacial phase will come into existence possessing a definite surface energy dependent on the composition of the two homogeneous liquid phases.

The study of the interfacial liquid-liquid phase however is complicated by several factors, of which the chief is the mutual solubility of the liquids. No two liquids are completely immiscible even in such extreme cases as water and mercury or water and petroleum; the interfacial energy between two pure liquids will thus be affected by such inter-solution of the two homogeneous phases. In cases of complete intersolubility there is evidently no boundary interface and consequently no interfacial energy. On addition of a solute to one of the liquids a partition of the solute between all three phases, the two liquids and the interfacial phase, takes place. Thus we obtain an apparent interfacial concentration of the added solute. The most varied possibilities, such as positive or negative adsorption from both liquids or positive adsorption from one and negative adsorption from the other, are evidently open to us. In spite of the complexity of such systems it is necessary that information on such points should be available, since one of the most important colloidal systems, the emulsions, consisting of liquids dispersed in liquids, owe their properties and peculiarities to an extended interfacial phase of this character.

2. Antonow's Rule.

A very significant observation connecting the interfacial tension between two liquid phases in equilibrium with the surface tension of each separately against the vapour phase was discovered by Antonow. The interfacial tension is equal to the difference between the two surface tensions. It is important to notice that we must deal with phases in equilibrium, since it often happens that the tension of the one pure liquid is greatly reduced by the addition of the second even though the solubility may be exceedingly small. In the extreme case, the solubility of one phase in the other is too small to be measured, as in the case of palmitic acid in water, but the surface tension of the solvent may, as we have already seen, nevertheless be reduced very much. The following examples* may be quoted in support of Antonow's rule.

Liquid	Surface tension			Interfacial tension		Temp. °C.
	Aqueous layer	Oil layer	Pure oil	Calculated	Observed	
Benzene	63·2	28·8	28·4	34·4	34·4	19
Ether	28·1	17·5	17·7	10·6	10·6	18
Aniline	46·4	42·2	41·9	4·2	4·8	26
Chloroform ...	59·8	26·4	27·2	33·4	33·3	18
Carbon tetrachloride	70·2	26·7	26·7	43·5	43·8	17
Nitrobenzene ...	67·9	43·2	43·4	24·7	24·7	18
Amyl alcohol ...	26·3	21·5	24·4	4·8	4·8	18
Cresol	37·8	34·3	37·1	3·5	3·9	18
Amyl alcohol 5 % + Benzene 95 % ...	41·4	28·0	26·0	15·4	16·1	17
Cresol 5 % + Benzene 95 % ...	56·5	28·7	29·1	27·8	27·5	17

The agreement in the above table is very good. Equally good are the results found by Reynolds in the case of benzene and aqueous solutions of various substances which raise the surface tension of water.

In certain cases the interfacial tension observed initially was close to the calculated value, but fell lower with lapse of time, sometimes considerably: thus with water and a liquid paraffin mixture the surface tensions of the two phases were respectively

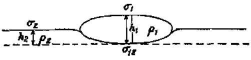
* Reynolds, *J.C.S.* cxix. 460, 1921.

73·0 and 31·5, and the interfacial tension fell from 41·0 after five minutes contact to 15·1 after standing together for a day. In such cases a chemical change may be assumed, although it is not always easy to find a probable one.

Solute	Concentration	Surface tension			Interfacial tension		Temp.
		Solution	Aqueous layer	Benzene layer	Calculated	Observed	
NaCl ...	0·1	72·2	64·0	28·9	35·1	34·9	18
" ...	1·0	74·4	65·5	28·7	36·8	37·3	19·5
" ...	5·0	83·5	72·0	29·1	42·9	42·5	17
NaOH ...	1·0	74·8	65·3	28·9	36·4	37·7	18
" ...	5·0	84·5	72·7	29·0	43·7	44·7	17
H_2SO_4 ...	0·5	73·0	62·5	28·0	34·5	35·0	25
" ...	2·5	75·6	65·7	28·9	36·8	36·6	18
" ...	5·0	77·4	66·2	28·9	37·3	37·1	18
$Na_2S_2O_3$	0·1	73·5	63·4	28·7	34·7	34·6	20
Glycerol	5·0	70·9	57·7	28·7	29·0	28·6	20
Sucrose...	0·1	73·7	62·7	28·7	34·0	34·4	20
" ...	1·0	75·3	63·0	28·9	34·1	34·1	18

(Concentrations measured in gm.-mols. per litre.)

Reynolds excepts from the general validity of Antonow's rule the tension of mercury and amalgams against certain electrolytes and immiscible liquids which react chemically. It is clear that the rule would be difficult to verify satisfactorily in the latter case; with mercury in contact with aqueous solutions (or with water) the apparent deviation from the rule is probably to be accounted for by consideration of the electro-capillary effects (Ch. VII).



If we consider the equilibrium of a lens floating on the surface of a mutually saturated liquid the following relationships evidently obtain

$$(1) \quad \sigma_2 + \tfrac{1}{2} g\rho_2 h_2^2 = \sigma_1 + \sigma_{12} + \tfrac{1}{2} g\rho_1 h_1^2,$$

$$(2) \quad g\rho_2 h_2 = g\rho_1 h_1.$$

Hence $$\sigma_2 - \sigma_1 = \sigma_{12} + \tfrac{1}{2} g h_1^2 (\rho_1/\rho_2)(\rho_2 - \rho_1).$$

Antonow's rule is thus only exact when the two mutually saturated liquids possess the same density. The observed values of σ_{12} should in general be slightly less than those determined from $\sigma_2 - \sigma_1$. In the case of oleic acid floating on water Devaux obtained a lens thickness of 0·1 cm. Since $\rho = 0{\cdot}90$ the interfacial surface tension should be 0·44 dyne less than the value obtained with the aid of Antonow's rule.

We may note that if we have the two liquids in separate vessels enclosed under one bell-jar so as to allow of free evaporation and condensation from one vessel to the other, the total surface tension in the vessel containing the liquid of higher tension will be unaltered if the other liquid distils over so as to cover the first with a thick film, for then we shall have two surfaces whose combined free energy equals that of the original surface. If on the other hand the liquid of higher tension were to distil over and form a thick film on the other liquid the sum of the surface energies would have increased by $\sigma_A + \sigma_{AB} - \sigma_B = 2\sigma_{AB}$ for each unit of surface; the phase of lower surface tension must therefore remain uncontaminated by the other.

3. Interfacial surface tension and solubility.

Since the interfacial tension between two liquids can always be expressed as the difference between two surface tensions, interfacial tensions in general must necessarily be smaller than surface tensions, and may be very small indeed. As a rule, especially with a closely related series of compounds, the interfacial tension increases as the solubility in the second liquid diminishes. Thus at 20° the interfacial tension of alcohols against water are

Propyl	alcohol	0 (miscible in all proportions)
Isobutyl	„	1·8
Isoamyl	„	4·4
Octyl	„	8·5

and the solubility diminishes in the same order.

Against mercury we have

Isobutyl alcohol	342·7
Secondary octyl alcohol	359·0

The order is the same, although the solubility of the liquids is so small as to be practically meaningless, so that solubility is not a helpful criterion in this case.

Let us denote by $\begin{cases} \sigma_A, \sigma_B \text{ the surface tensions of the pure liquids,} \\ \sigma_{A'}, \sigma_{B'}, \text{ those of the mutually saturated phases,} \\ \sigma_{AB} \text{ the interfacial tension.} \end{cases}$

Then by Antonow's rule, $\sigma_{AB} = \sigma_{A'} - \sigma_{B'}$.

Now if the mutual solubility be not great, $\sigma_{B'}$ will not differ much from σ_B: $\sigma_{A'}$ may however be very much less than σ_A, and the difference will as we have seen be greater the larger the surface concentration of B when dissolved in A. Thus the effect of B in lowering the surface tension of A against air is reflected again in the interfacial tension between the two liquids.

4. Influence of temperature.

The variation of interfacial tensions with temperature has been measured by Harkins in the case of a few organic liquids against mercury, and like surface tensions they diminish with rise of temperature.

Liquid	0°	10°	20°	30°	40°	50°	
Iso-butyl alcohol ...	349·1	345·6	342·7	341·0	340·2	339·3	Interfacial tension against mercury
Secondary octyl alcohol...	365·4	361·7	359·0	357·3	355·0	353·6	
Octane	377·2	375·8	374·7	373·4	372·6	371·3	
Benzene	—	361·3	357·2	353·7	351·4	349·8	
Surface tension of mercury	480	478	476	474	471	469	

The decrease of interfacial tension with rising temperature might normally be ascribed to increase in solubility. We have unfortunately no data with which to compare the interfacial tensions directly with solubility of a pair of partially soluble liquids at different temperatures, but from the results of Whatmough* on the surface tensions of such phase pairs we can calculate the interfacial tensions from Antonow's rule. The following values are interpolated from his results.

* *Zeit. Phys. Chem.* xxxix. 129, 1902.

ANILINE AND WATER.
(Critical solution temperature = 168° C.)

Temp. ° C.	15	25	35	45	55	65	75
Tension of aqueous phase	59·92	59·000	58·155	56·965	55·485	54·64	53·505
Tension of aniline phase	54·64	53·795	52·615	51·520	50·140	49·01	47·830
Interfacial tension calculated ...	5·28	5·205	5·540	5·445	5·345	5·63	5·675

METHYL ALCOHOL AND CARBON DISULPHIDE.
(Critical solution temperature = 40·5° C.)

Temp. ° C.	10	20	30	38·8
Tension of CH_3OH phase ...	27·49	26·51	25·44	24·66
Tension of CS_2 phase... ...	27·75	26·67	25·49	24·66
Interfacial tension calculated	0·26	0·16	0·05	0·00

(Mean temperature coefficient of interfacial tension 0·0009.)

Goard and Rideal obtained the following values for the surface tensions of mutually saturated solutions of phenol and water.

PHENOL AND WATER.
(Critical solution temperature = 68·8° C.)

Temp. ° C.	0	10	20	30	40	50	60
Tension of aqueous phase	41·479	40·650	39·880	39·200	38·582	38·10	36·70
Tension of phenol phase	41·865	41·000	40·220	39·495	38·836	38·24	36·73
Interfacial tension calculated ...	0·386	0·350	0·340	0·295	0·254	0·14	0·03

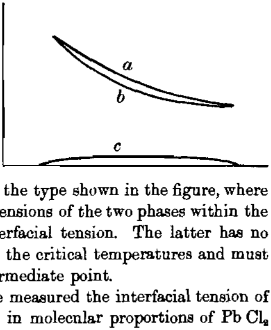
It is a characteristic of two component systems forming one phase at a certain temperature that at this temperature the curve relating the partial molal free energy to the relative concentration of the components becomes horizontal. In other words at the critical point

$$\frac{d\mu}{dN} = 0.$$

Since however $\Gamma = -\frac{d\sigma}{d\mu}$, or $-\left(\frac{d\sigma}{dN}\right)_A \left(\frac{dN}{d\mu}\right)_A$, it follows that for

Γ to assume a finite value $\frac{d\sigma}{dN}$ must also be zero. Thus as pointed out by G. N. Lewis (*Thermodynamics*, p. 253) at the critical point "a small change in composition will not change the surface tension between the liquid and air, regardless of the amount of surface adsorption of either constituent of the liquid." In addition since for some distance on either side of the critical point the variation of the partial molal free energy with the composition is small unless the surface adsorption exhibits violent changes the surface tension is largely independent of the composition.

In these examples, as one would expect, the interfacial tensions are small and diminish as the critical solution temperature is approached. The differences between the surface tensions of the two phases are generally too small to decide whether the interfacial tension approaches zero asymptotically in all cases although such appears to be the case in the phenol water system: we notice however that the temperature coefficient is very small indeed, as is the case for surface tensions of liquids near their critical point, but to a still greater degree. It would be of considerable interest to have data for the surface and interfacial tensions of a pair of liquids such as nicotine and water which are miscible in all proportions except within a definite temperature range. Here we should expect to find curves of the type shown in the figure, where a and b represent the surface tensions of the two phases within the critical region and c their interfacial tension. The latter has no meaning either above or below the critical temperatures and must have a maximum at some intermediate point.



Lorenz and Liebmann* have measured the interfacial tension of molten lead against a mixture in molecular proportions of $PbCl_2$ and KCl between 450° and 600°. The results may be expressed approximately by the formula $\sigma = 211 + 0{\cdot}147\,(600 - t)$, though considerable experimental errors make the figures somewhat uncertain.

* *Zeit. Phys. Chem.* LXXXIII. 459, 1913

In bringing together the surfaces of two liquids to form a liquid-liquid interface heat is either evolved or absorbed during the process. This heat change may be termed with Harkins the heat of adhesion. The sum total of the surface energies of the two surfaces before contact less that of the interface after contact represents this total amount of energy given off or absorbed if the process be carried out isothermally or

$$Q=\left\{\sigma_1-T\frac{d\sigma_1}{dT}+\sigma_2-T\frac{d\sigma_2}{dT}\right\}-\left\{\sigma_{12}-T\frac{d\sigma_{12}}{dT}\right\}.$$

Harkins gives the following values for the heats of adhesion of the following interfaces:

Interface	Heat evolved in calories per sq. cm.
Water-hexane ...	$2{\cdot}6\times10^{-6}$
Water-octyl alcohol	$4{\cdot}0\times10^{-6}$
Water-carbon tetrachloride ...	$2{\cdot}5\times10^{-6}$

In the case of octyl alcohol the area of a molecule is *ca.* 25 Å. Thus a gm. molecule of octyl alcohol would occupy some $1{\cdot}51\times10^{9}$ sq. cms. and the heat evolved would thus be of the order of 6000 calories per gm. molecule. If the liquid-liquid interface be formed by the condensation of a vapour on the clean surface of a liquid (σ_1) the heat of adsorption will be

$$Q=\left\{\sigma_1-T\frac{d\sigma_1}{dT}\right\}+\lambda v-\left\{\sigma_{12}-T\frac{d\sigma_{12}}{dT}\right\},$$

where λ is the latent heat of vaporisation of the liquid which is condensed from the vapour phase. Harkins finds values of 3·25 and $3{\cdot}13\times10^{-6}$ calories per sq. cm. for the heat of adsorption of isobutyl alcohol and octane respectively on a water surface.

Interfacial surface tension and chemical constitution.

Some interesting conclusions may be drawn from a consideration of the magnitude of the interfacial surface tensions of various liquids. The significance of these was first pointed out by Hardy (*Proc. Roy. Soc.* A, LXXXVIII. 303, 1913) and emphasised by Harkins (*J.A.C.S.* XXXVIII. 228, 1916; XLII. 700, 1920). We have noted that Antonow's rule only applies to mutually saturated solutions. If two

pure liquids be brought in contact with one another in general

$$\sigma_A + \sigma_B > \sigma_{AB},$$

or during the process of mutual saturation as would be anticipated there will be a decrease in the free energy of the system. The magnitude of this decrease in the free energy is a measure of the chemical work performed and has an important bearing on the nature of the two liquids.

Harkins defines two terms, the work of cohesion W_c which is the work done when a bar of liquid of unit cross sectional area is pulled apart against the cohesive forces. It is thus numerically equal to twice the surface energy of the liquid. The work of adhesion W_a is similarly defined as the work required to pull apart a composite bar consisting of half of one liquid and half of the other, at the place of junction.

W_a is evidently defined by the decrease in free energy when the two liquids are brought into contact

$$W_a = \sigma_A + \sigma_B - \sigma_{AB},$$

$W_c = 2\sigma_A$ for the first liquid and $2\sigma_B$ for the second.

Thus

for water	$W_c = 145{\cdot}8$ ergs per sq. cm.
for octane	$W_c = 43{\cdot}5$ „ „ „ „
for octane-water	$W_a = 43{\cdot}8$ „ „ „ „
for octyl alcohol	$W_c = 55{\cdot}1$ „ „ „ „
for octyl alcohol-water	$W_a = 91{\cdot}8$ „ „ „ „

According to Harkins' views, on breaking a bar of octyl alcohol the molecules of the alcohol on both sides of the plane of break should orientate themselves so that the break would occur with the least possible expenditure of work; in this case the molecules should orientate themselves so that the final break can occur between the ends of the hydrocarbon chains. This should lead to a value of W_c equal to that of octane. The higher figure actually observed Harkins attributes to imperfect orientation due to thermal agitation.

In the case of the octyl alcohol-water interface the hydroxyl groups of the alcohol are immersed in the water, consequently when a bar of octyl alcohol is pulled away from the water, polar groups must be pulled from polar groups, so a high value of the work of adhesion should result from the orientation at such an interface.

It thus follows that the difference between W_c for an organic liquid and W_a for that liquid and water should be a measure of the asymmetry of the molecules of the former. Compounds containing polar groups should give higher values for $W_a - W_c$ as is exemplified by the following data.

Liquid	$W_a - W_c$ for water liquid interface in dynes per cm.
n-Hexane	9·44
n-Octane	0·22
Methyl alcohol ...	50·10
Propyl alcohol ...	51·10
Ethyl ether ...	45·50
Acetic acid	45·20
Carbon tetrachloride	2·83
Ethyl bromide ...	17·44
Benzene	8·91
Toluene	6·84
Aniline	24·45
Nitrobenzene ...	3·76
Benzaldehyde ...	17·25

The interfacial surface tension may be markedly affected by a surface reaction occurring in the presence of traces of impurities. A good example of such an effect is to be noted in the alteration of the interfacial surface tension between an oil containing a fatty acid and water containing acid or alkali. For acid solutions the interfacial surface tension remains constant and almost independent of the P_H of the aqueous phase. As the solution becomes more alkaline the carboxyl groups of the acid commence to dissociate and the interfacial surface tension falls rapidly. (Hartridge and Peters, *Proc. Roy. Soc.* A, CI. 348, 1922, see p. 252.)

5. Interfacial tension of solutions.

In the case of the interfacial tension of two pure liquids we have had to deal with the superficial system in equilibrium with a two phase two component system of three dimensions. If we add to this system a third component the problem becomes still more complicated. The simplest case is that in which the added substance is soluble in one phase and completely insoluble in the other, the original liquids being themselves mutually insoluble. The change of interfacial tension should then run parallel to the change of surface tension of the liquid in which the third component dissolves.

If the original liquids are mutually soluble and the third component is soluble in only one of them, the mutual solubility will be diminished by its addition—according to Nernst's law, at low concentrations. The rise or fall of interfacial tension will thus depend on two superimposed effects, the change of surface tension of the better solvent owing to addition of the solute, and that in each of the two liquids due to diminished concentration of the other. The latter effect tends to increase the tension while the former may work in either direction.

If the original liquids are again partially miscible, and the added component soluble in either the mutual solubility may be increased; if so the interfacial tension will probably diminish whatever may be the effect on the surface tensions of the two pure liquids. Clearly, if sufficient of the third component be added to make the two phases completely soluble the interfacial tension must disappear altogether.

It is logical to conclude with the case where the new component is not appreciably soluble in either phase. At first sight it would appear unlikely that the interfacial tension could then be affected in either direction, yet this is possible. If the interfacial tension is increased by its addition to the system this substance will be adsorbed at the interface; if decreased, the added body will be more sparsely distributed at the interface or not appear there at all. It is easy to observe, at any rate, the appearance of a film of non-transparent matter at the interface, and the experiment has been carried out for a number of liquid pairs and solids by Hofmann. (*Zeit. Phys. Chem.* LXXXIII. 385, 1913) and by Reinders (*Koll. Zeit.* XIII. 235, 1913). Powders of different kinds of insoluble inorganic compounds were shaken up with water and an organic liquid: in a few cases the powder went completely into the aqueous phase, in much fewer the organic liquid contained practically all the suspension, but in the great majority the solid went preferentially or completely to the interface. We should conclude then that the interfacial tensions involved are diminished by the addition of most inorganic solids. The argument is not perfectly complete since the particles are comparatively so large that we ought also to consider the tension at each of the solid-liquid surfaces. To begin from another side, the solid will go to the interface if each liquid is adsorbed at the surface between the solid and the other liquid, that

is to say if the mutual solubility is increased at the surface of the solid. (The case is very similar to that of catalysis at a solid surface.) The positive adsorption of the first liquid A at the surface of the solid S and the second liquid B will occur if the tension S/A is diminished by B: similarly the tension S/B must be diminished by A. But $A/B = S/A \sim S/B$, hence if A be the liquid with the higher interfacial tension against S, S/A must be lowered by B to a greater extent than S/B by A. The necessity for considering the solid-liquid interfaces become less when the solid particles are of less than three dimensional magnitude as in the case of suitable colloidal solutions. Reinders found that colloidal gold solutions went to the interface when shaken with CS_2, ether or isobutyl alcohol: here probably we may simply say that the effect is due to a lowering of the interfacial tension. A dilute solution of gelatine goes to the interface when shaken with benzene.

As examples of the first case we may consider McLewis' (*Phil. Mag.* (6), XVII. 466, 1909) results for the interfacial tension of petroleum against aqueous solutions of metallic salts (and of organic substances). He found that lowering of the interfacial tension occurred with addition of $CuCl_2$, $AgNO_3$ or KCl—an unexpected result, since each of these substances raises the surface tension of water against air, and presumably does not influence that of the organic liquid, so that the interfacial tension might be expected to be raised. This case deserves closer investigation. That aqueous sodium glycocholate should lower tbe interfacial tension of the same is to be expected, since this salt is adsorbed also at an air-water interface. Similarly Harkins found that butyric acid lowers the surface tension water-benzene: the maximum quantity of solute adsorbed at the interface agreed with that at a water-air interface. Strictly, this example should come into the second class, since the solute is soluble in both solvents.

The interfacial tensions of a number of aqueous solutions against mercury have been measured by McLewis *, Patrick and others. The tension was lowered by addition of all the solutes examined, including mercurous sulphate, salicylic acid, picric acid, neofuchsin, morphine hydrochloride, caffeine, aniline, sodium glycocholate. All of these substances except mercurous sulphate lower the surface

* See p. 36.

tension of water, yet diminish at the same time the interfacial tension against mercury. It would be interesting to examine the effect of traces of these bodies on the surface tension of mercury, for if Antonow's law holds good the surface tension of mercury should be lowered by them even more than that of water. We should, in fact, expect to find contamination of the mercury surface due to adsorption. In no case does the interfacial tension of mercury appear to be raised by the addition of a solute to water and qualitatively this fact agrees well with the well-known ready contamination of mercury surfaces.

The most accurately determined example of the third class has already been cited, namely the effect of butyric acid on the interfacial tension benzene-water. Harkins has found the concentration of acid in both layers for each pair of phases in equilibrium, but did not measure that of the second solvent. The mutual solubility must however almost certainly increase with the addition of a body soluble in either, but the interfacial tension is still diminished, adsorption of the solute counterbalancing the greater resemblance of the two phases. Bubanovic* has also determined the interfacial tensions of the same solutions against olive oil, obtaining very similar results. He has also examined solutions of chloral hydrate.

On the other hand the surface tension of water against olive oil is practically unaltered by the addition of ethyl alcohol, chloroform, benzene, or xylene, all of which lower to a greater or less degree the surface tension of water against air, and in these examples we may conclude that the greater mutual solubility has had at least as great an effect on the tension as the tendency to adsorption of the solute. An interesting experiment would be to start with two partially miscible liquids and add a third which would finally yield complete miscibility, following changes of composition and interfacial tension simultaneously. A similar result would be achieved by taking for example a concentrated aqueous solution of ammonia and adding potassium carbonate until two phases were reached, one rich and one poor in this salt.

Meyer† has measured the interfacial tension of amalgams of the alkali metals against aqueous solutions of their salts, obtaining

* *Meddel. fr. K. Vetensk. Nobelinstitut*, II. 17, 1911.

† *Zeit. Phys. Chem.* LXX. 321, 1910.

results similar qualitatively to those of Schmidt* for the surface tensions against air. The interfacial tension mercury-normal KOH is reduced to 33 °/₀ of its value by the addition of 0·0224 °/₀ of potassium to the metal, and when the concentration of potassium is only 0·0011 °/₀ by weight the tension has already fallen to 54 °/₀. In the case of sodium amalgam-normal Na_2SO_4 the surface activity is still more striking: for lithium amalgam-normal LiCl it is not quite so great. (Although lithium does not appear to lower the surface tension of mercury against air.)

Meyer's results also resemble those of Schmidt in the peculiarity that the rapid fall in the value of the surface tension does not begin at the very lowest concentrations of solute. The first addition of alkali metal indeed produces little effect on the interfacial tension, and there is a point of inflexion on the concentration surface tension at its steepest part. This behaviour appears to be characteristic of amalgams: the explanation is not clear and the phenomenon deserves further investigation.

6. Emulsions.

The emulsions consist of two liquid phases, one, the disperse or discontinuous and the other the dispersion medium or continuous phase. It is evidently possible to obtain with one pair of immiscible liquids two emulsions the one the invert of the other with respect to the continuous and discontinuous phases. We have noted that the interfacial energies of immiscible liquids such as water and aniline although not so large as are the computed values for solid-liquid interfaces are by no means inconsiderable and may be as high as 30–40 ergs per sq. cm. whilst even higher values are obtainahle when one liquid is a metal such as mercury. Such liquids when dispersed in water form exceedingly unstable emulsions comparable to the suspensions (see Ch. v). The volumnar ratio of the phases does not readily exceed 1 in 1000 and eventual coalescence on contact due to thermal agitation, i.e. the Brownian movement, usually occurs relatively rapidly. Dilute emulsions in water thus prepared are negatively charged and exhibit the phenomenon of electric endosmose whilst they are relatively easily precipitated by the addition of electrolytes in which the cations

* *Zeit. f. Phys.* xxxix. 1108, 1912.

are the effective precipitating agents. The volumnar ratio of the disperse phase may however be increased, and the emulsions rendered more stable with the aid of addition or emulsifying agents. Such emulsifying agents can increase the stability of an emulsion in two ways (1) by the formation of a film round the disperse phase which on account of its mechanical strength prevents coalescence on contact and (2) by lowering the interfacial surface energy to small values thus reducing the tendency to coalescence. The emulsifying agent must consequently be one that goes to the interface between the two liquids, impart to the interface mechanical strength and effect a marked lowering of the interfacial surface tension.

7. Limits of emulsions.

The disperse phase consisting of relatively minute drops if imagined to be perfectly spherical and undeformable would, when increased in number or size until point contact between neighbouring spheres was obtained, yield a volumnar ratio of disperse phase to dispersion medium of 74 : 26 which would fix automatically the upper limits possible in emulsification. The experiments of S. U. Pickering however (*J.C.S.* XCI. 2002, 1902) have indicated that much higher values for the volumnar ratio may be obtained, thus with suitable emulsifying agents such as soap, paraffin could be dispersed in water until a volumnar ratio of 99 : 1 was obtained. The logical interpretation of the experiments is to assume that the disperse oil drops are not undeformable but may be flattened at the points of contact as the spheres grow in number or in size, until ultimately the dispersion medium is reduced to a thin film enclosing a number of pentagonal dodecahedra. For such an intimate contact, where the surfaces of the polyhedra are formed by means of a film, to he stable it is evident that the emulsifying agent must possess great mechanical strength but must at the same time not be too brittle otherwise fracture may result and the emulsion be broken.

We should thus expect that such emulsions would be rigid, and actually they set to a stiff jelly-like consistency. These emulsoid jellies or greases are polyhedral in structure and are to be dis-

tinguished from the true "gels" which consist of a solid disperse phase in a liquid dispersion medium (see Ch. IX).

8. **The emulsifying agent.**

It has already been indicated that two types of emulsions may be obtained between two immiscible liquids *A* and *B*, the one consisting of *A* dispersed in *B* the other of *B* dispersed in *A*. In order to impart the requisite degree of stability to such systems an emulsifying agent must be added such that it will lower the surface tension of such liquid and thus in accordance with the Gibbs' equation go to the interface and there produce a film which possesses a certain amount of mechanical rigidity. Substances which exist in colloidal solution and effect a marked lowering of the interfacial surface tension may actually undergo coagulation to form a solid membrane at the liquid interface. Such membrane formations have been noted both at liquid-air interfaces and also at liquid-liquid boundaries; thus saponin (Ramsden, *Proc. Roy. Soc.* A, LXXII. 156, 1903) separates out at a large water-olive oil interface, cellulose nitrate at a benzene-water interface (Holmes and Cameron, *J.A.C.S.* XLIV. 66, 1922) and gelatine at an oil-water interface (Nugent, *Trans. Farad. Soc.* XVII. 703, 1922). The discrepancy between the actual amount of emulsifying agent adsorbed at the interface and that calculated with the aid of the Gibbs' equation has been shown (*loc. cit.*) to be due partly to the non-ideal character of the emulsifying agent in solution, e.g. colloidal soaps and dyes, and partly to the high surface concentrations obtained which we have noted approximate to a limit of saturation above which precipitation and other irreversible changes frequently occur. The nature of the emulsion is found to depend on the emulsifying agent employed; thus soaps on addition to oil and water produce an oil in water emulsion whilst the calcium salts of the fatty acids produce the invert emulsion of water in oil. In the same way the solid basic sulphates of iron, copper and metal are effective in producing oil in water emulsions but soot produces the invert water in oil emulsion.

The stability of an emulsion is dependent on the amount of the emulsifying agent at the interface. Briggs (*Jour. Phys. Chem.* XIX. 210, 1915) has examined the adsorption of sodium oleate at

a benzene-water interface by determining the amount of soap extracted by emulsification of the benzene and thus increasing the liquid-liquid interface, when the following figures were obtained.

Conc. soap gms. per litre	gms. sodium oleate adsorbed per litre of benzene
0·60	0·17
1·18	0·28
3·18	0·40
6·36	0·44
13·85	0·48
21·03	0·49
26·01	0·54

These figures are in approximate agreement with values calculated with the aid of the Freundlich adsorption isotherm (see p. 134) but no definite conclusions may be drawn from them since the actual area of liquid-liquid interface in all probability was variahle being dependent on the amount of emulsifying agent present. More recently the quantity of various soaps required to form a stable emulsion of kerosene in water has been determined by Griffin (*J.A.C.S.* XLV. 1648, 1923) for sodium oleate, potassium stearate and potassium palmitate and by der Meulen and Riemann (*ibid.* XLVI. 876, 1924) for sodium ricinoleate.

The general method of procedure was to disperse a known volume of paraffin in water with the aid of the soap. The average diameter of the kerosene emulsion droplets was determined by counting with the aid of a microscope and hemacytometer, from which the total interfacial area could be calculated.

The emulsion was then allowed to separate and it was found on analysis of the soap content of the aqueous lower layer and the concentrated emulsion in the upper layer that the emulsion had abstracted soap from the solution. Owing to the fact that the fatty acids are soluble in the oil the hydrolysis of the soaps and the subsequent removal of the fatty acid in the oil phase had to be eliminated by the addition of caustic soda. In this way the true quantity of soap at the oil-water interface could be determined. Some of the results obtained are tabulated below.

	Conc. of soap mols. per litre	Conc. of base mols. per litre	Acid at interface mols. per litre	Area of interface × 10^{-3} per c.c. of oil in sq. cm.	Area of interface occupied by 1 molecule of soap Å.
Potassium stearate	0·100	0·01	·0043	7·60	29
Potassium palmitate	0·010	0·01	·0040	7·60	31
Sodium oleate ...	0·100	0·01	·0028	7·45	44

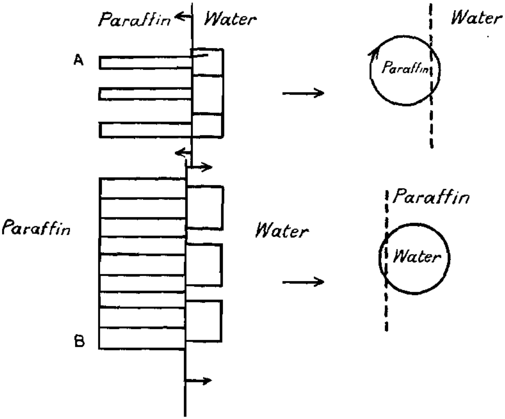
As a result of a number of experiments the mean areas of paraffin-water interface occupied by a molecule of the emulsifying soaps were obtained as follows. For comparison Langmuir's values for the actual areas of the fatty acids are appended whilst Adam's value for the —COOH head is 25·1 Å.

	Mean area in Å.	Actual area of fatty acid Å.
Sodium oleate ...	48	46
Potassium stearate	27	22
Potassium palmitate	30	21
Sodium ricinoleate	from 39·2 to 105·6	

It was found that if less soap were employed the emulsions were unstable. The experimental results agree with the conclusion that the soaps exert their emulsifying powers on oil-water mixtures by going to the interface and coating the interface with a layer of soap one molecule deep.

Furthermore from the computed area of the cross-section of the interface occupied by one soap molecule it is clear that the molecules of the soap are relatively close together and orientated in a plane at right angles to the interface. As has already been noted in the case of the air-water interface the fatty acids are orientated with their polar carboxyl groups in the water phase; we would consequently anticipate that in the oil-water interface the same orientation would occur, the hydrocarbon chain being immersed in the paraffin phase and the polar —COONa or —COOK group in the aqueous phase. Such orientation is an important factor in the

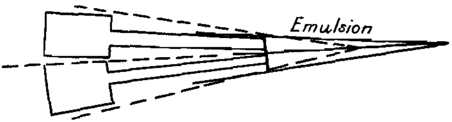
type of emulsion produced by the emulsifying agent, as is evident from a consideration of the two cases *A* and *B* in which orientated molecules possessing a non-polar portion immersed in the paraffin and a polar portion in the aqueous phase are represented as orientated in a compressed orientated unimolecular layer at a paraffin-water interface. In the first case *A* the polar head is represented as possessing a cross-section considerably larger than



that of the non-polar portion to which it is attached. In *B* the converse is the case. It is clear that the ingress of more soap molecules into the interface would necessitate an increase in the water surface in case *A* and of the paraffin surface in *B*. Since these two surfaces are already tightly packed, the mobile interface thus bends in the direction of the arrows, thus forming an oil in water emulsion in the first case and the invert water in oil emulsion in the second.

Thus the type of emulsion formed depends essentially on the relative cross-section areas of the non-polar and polar portions of

the emulsifying agent. Furthermore if we represent diagrammatically the cross-section of two soap molecules in juxtaposition to one another at the interface of an oil in water emulsion as follows it is clear that the curvature of the interface or fineness of the emulsion



is dependent on three factors, the cross-section of the head or polar end, the —COONa group, the cross-section of the non-polar portion or hydrocarbon chain and the length of the molecule. The influence of the cross-sectional areas of the molecular heads and tails on both the nature and the fineness of emulsions has been examined by Finkle, Draper and Hildebrand (*J.A.C.S.* XLV. 2780, 1923) in an investigation on the emulsifying powers of the stearates and oleates of the metals. Although no actual computation of the cross-sectional area of the various metal carboxylate —COOM groups when dissolved in water and possibly solvated could be made, yet the relative sizes can be inferred from a consideration both of the atomic volumes and of the atomic diameters as determined by the method of X-ray analysis. The type of emulsion and these constants for the metal ion in metal oleate as emulsifying agent are given in the following table:

Metal ion	Atomic diameter Å.	Atomic volume	Type of emulsion
$Cs^{\cdot}$ ...	4·75	70·6	Oil in water
$K^{\cdot}$ ...	4·15	45·3	
$Na^{\cdot}$ ...	3·55	22·9	
$Ag^{\cdot}$ ...	3·55	10·3	Water in oil
$Ca^{\cdot\cdot}$ ...	3·40	12·6	
$Mg^{\cdot\cdot}$ ...	2·85	7·0	
$Zn^{\cdot\cdot}$ ...	2·65	4·6	
$Al^{\cdot\cdot\cdot}$ ...	2·70	3·4	
$Fe^{\cdot\cdot\cdot}$ ...	2·80	2·3	

The cross-section of the heads when dissolved in water —COOCs, —COOK, —COONa are evidently greater than the cross-section of the hydrocarbon oleate chain, whilst the head —COOAg is smaller than the chain since the invert emulsion is produced. Similarly the groups

$$\left.\begin{matrix}\mathrm{-COO}\\\mathrm{-COO}\end{matrix}\right\rangle\mathrm{Ca},\quad \left.\begin{matrix}\mathrm{-COO}\\\mathrm{-COO}\end{matrix}\right\rangle\mathrm{Mg},\quad \left.\begin{matrix}\mathrm{-COO}\\\mathrm{-COO}\end{matrix}\right\rangle\mathrm{Zn},$$

have a smaller cross-section than two oleic acid molecules, whilst the polar groups containing the trivalent elements iron and aluminium would possess cross-sections smaller than three oleate molecules.

Both the stability and curvature of the emulsions are dependent on the head sizes as is indicated from the following figures for the stability and mean diameter of benzene-water emulsions emulsified with various metallic oleates.

OIL IN WATER.

Metal soap ...	Cs	K	Na
Life of emulsion	8 weeks	8 weeks	6 weeks
Mean diameter of emulsion particle	·0029 mm.	·0039 mm.	·0055 mm.

WATER IN OIL.

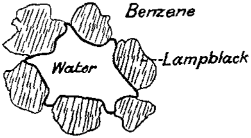
Metal soap ...	Ca	Ag	Mg	Zn	Al	Fe
Life of emulsion	1 hour	1 day	2 days	24 days	7 days	10 days

No data are as yet available on the effect of length of tail on the emulsion size. As has already been noted (p. 46) fatty acids with short hydrocarbon tails are very water soluble and the sodium soaps soluble to a greater degree, interfacial adsorption is consequently small. Thus the concentration required to produce a saturated film at the oil-water interface will be correspondingly greater. This necessitates a high sodium ion concentration in the

aqueous phase which although weakly adsorbed by the electro-negative oil drops may rise to those concentrations where discharge of the emulsion droplets occurs before the protective film has been formed.

The precipitating action of the sodium ions thus exceeds the protective action of the adsorbed sodium salts for short hydrocarbon chains, but as the chain gets longer and the interfacial adsorption increases the specific influence of the ion precipitation rapidly decreases.

Emulsification produced by the addition of a dispersed solid to the two liquid phases must likewise be imagined to take place by reason of the solid going to the dineric surface (see p. 106) and being wetted but possessing a different angle of contact for each liquid. A microscopic examination of water emulsified in benzene stabilised with lamp black indicated that this was actually the case.



Evidently the lamp black is more soluble in the benzene than in the water phase. On increasing the concentration of lamp black in the mixture the curvature of the particles increases and the mean diameter of the emulsion decreases as noted by Moore (*J.A.C.S.* XLI. 944, 1919) who obtained the following figures. The

Weight of lamp black per 10 c.c. kerosene in 30 c.c. N.NH_4Cl (grms.)	Mean diameter in mm.
0·4	·0551
0·6	·0452
0·8	·0367

above arguments explain Bancroft's rule that a colloid emulsifier causes the phase in which it is soluble to be the external phase.

Donnan and Potts (*Zeit. Koll.* IV. 208, 1910) showed that the interfacial surface tension of a hydrocarbon water surface was

lowered by the sodium soaps of the fatty acids and the lowering was dependent on the length of the chain as indicated by the following data.

Na salt of	Relative interfacial surface tension of oil-water interface referred to unity							
	$\frac{N}{400}$	$\frac{N}{200}$	$\frac{N}{100}$	$\frac{N}{80}$	$\frac{N}{40}$	$\frac{N}{25}$	$\frac{N}{20}$	$\frac{N}{10}$
Acetic ...	—	—	·995	—	·970	—	·937	·876
Propionic ...	—	—	—	—	·946	—	·901	·827
Butyric ...	—	—	—	—	·945	—	·909	·856
Valeric ...	—	—	—	—	—	·946	·908	·821
Heptylic ...	—	—	—	—	·939	—	—	·754
Caproic ...	—	—	—	·947	·921	—	·869	·780
Caprylic ...	·962	—	·895	—	·797	—	—	—
Capric ...	—	—	—	·835	·730	·630	—	—
Nonylic ...	·911	·856	·798	·753	·656	—	—	—
Lauric ...	—	·698	·532	·474	—	—	—	—
Myristic ...	·585	—	—	—	—	—	—	—

Although all the sodium salts are, as is indicated by the lowering of the surface tension, adsorbed at the interface the concentrations necessary to effect emulsification are so great for the salts of the short chain fatty acids that precipitation by the sodium ions results before the protective film can be built up. The first signs of emulsification are noted in the case of sodium caprate and sodium nonylate coinciding with the appearance of colloidal properties on solution.

9. The Phase Inversion.

The fact that sodium salts of fatty acids will form an oil in water emulsion whilst the addition of calcium salts yields a water in oil emulsion is as we have noted explicable on the hypothesis that the cross-section of the hydrated —COONa is greater, whilst the hydrated $\begin{matrix}\text{—COO}\\\text{—COO}\end{matrix}\!\!>\text{Ca}$ is less, than the cross-section of one and two hydrocarbon chains respectively. On the addition of both sodium and calcium salts to the oil-water mixture it is evident that with suitable adjustment of the sodium soap to calcium soap ratio in the aqueous phase a condition of affairs may be reached such that the composition of adsorbed mixed soap at the dineric surface may be so adjusted as to give equal areas on each side of the interface. This state was

first realised by Clowes (*Jour. Phys. Chem.* XXIX. 407, 1916) who showed that with a sodium to calcium soap ratio equal to 4 : 1 (in molar ratio) the emulsion was unstable, a slight excess of sodium ions converting it into the oil in water type, a slight excess of calcium ions resulting in a water in oil emulsion. On the hypothesis of a unimolecular orientated soap film, indicated above, we must imagine that the interfacial film contains both adsorbed sodium soap in molecules per sq. cm. and calcium soap in molecules per sq. cm., in such a proportion that the mean area of n sodium carboxylate and m calcium carboxylate heads is equal to the cross-section of $n + 2m$ hydrocarbon chains. The inversion point is readily determined by the abrupt rise in electrolytic conductivity when the continuous oil phase is inverted to the continuous electrolyte containing water phase.

The inversion point of a number of salts for such emulsions has been investigated by Bhatnagar* (*J.C.S.* CXVII. 542, 1920), but unfortunately no data on the interfacial adsorption of the mixed salts are available as yet.

Some of Bhatnagar's data are tabulated below.

Emulsion: 10 c.c. water, 10 c.c. oil.
Emulsifying agent: potassium oleate.

Amount of soap in millimols.	Millimols. salt added to invert the emulsion				
	$Ba(NO_3)_2$	$Ca(NO_3)_2$	$Pb(NO_3)_2$	$Cr_2(SO_4)_3$	$Al_2(SO_4)_3$
0·080	2 × ·0199	2 × ·020	2 × ·0198	·017	·017
0·100	2 × ·0281	2 × ·027	2 × ·0252	·019	·017
0·151	2 × ·0410	2 × ·042	2 × ·0400	·028	·025
0·162	2 × ·0421	2 × ·044	2 × ·0440	·030	·027

According to his data the power of the various ions to reverse the phases followed the following order:

$$Al^{\cdot\cdot\cdot} > Cr^{\cdot\cdot\cdot} > Ni^{\cdot\cdot} > Pb^{\cdot\cdot} > Ba^{\cdot\cdot} > Sn^{\cdot\cdot},\ Ca^{\cdot\cdot}.$$

The explanation of stabilisation and phase inversion advanced above has as been noted received support from the experimental data on the effect of soaps and the salts of the fatty acids.

Emulsions can however be stabilised and inverted by the

* *Trans. Farad. Soc.* XVI. 27, 1921.

addition of salts of the inorganic and simpler organic acids. Thus with olive oil and water Clowes (*Koll. Zeit.* xv. 123, 1914) noted a phase inversion from oil in water to water in oil with the following salt pairs the second salt producing the invert water in oil emulsion.

Salt pair		Mol. ratio at inversion point
NaOH	$Cu(OH)_2$	2 : 1
Na citrate	$CaCl_2$	2 : 1
NaOH	$CaCl_2$	4 : 1
NaCl	$CaCl_2$	100 : 1
KCl		

We have already referred to the experiments of Bhatnagar on the effect of inorganic salts on phase inversion of paraffin emulsions stabilised with soaps and similar conclusions have been arrived at by Parsons and Wilson (*J. Ind. Eng. Chem.* XIII. 1119, 1921) utilising a purified mineral oil. They state however that no critical ratio of magnesium to sodium oleate could be obtained at which the emulsion was at the inversion point since two emulsions, the one the invert of the other, were always obtained. The work of Baur (see p. 119) has demonstrated quite clearly that the inorganic ions are oil soluble and that the difference between the partition ratios of cation and anion between oils and water may give rise to interfacial potential differences as well as interfacial concentration differences of cation and anion on each side of the interface. The difficulty of obtaining stable emulsions with a fat free paraffin and inorganic soluble salts indicates however that these effects are relatively unimportant compared with those obtained with molecules which are definitely non-polar in character but containing a polar group. It is thus probable that the varying ratios of salts obtained for the inversion points with water-oil systems where the oil consists of a glyceride of a fatty acid are to be attributed to metathesis of the salt with traces of fatty acids present in the oil resulting in the production of soaps rather than the specific ionic adsorption. A careful examination of the emulsifying powers of inorganic salts on benzene or paraffin oil-water systems from which all traces of fatty acids or alcohols have been removed is evidently desirable in

this connection. We find for example that neither Briggs (*J. Ind. Eng. Chem.* XIII. 1009, 1921) nor Harkins (*J.A.C.S.* XXXVIII. 242, 1916) could obtain any evidence for any stabilising action of sodium chloride in a water-benzene mixture. In commercial olive oil however a noticeable stabilisation is obtained but the aqueous solution becomes slightly acid as would be anticipated if metathesis occurred with simultaneous adsorption of the liberated soap

$$NaCl + C_nH_{2n+1}COOH \rightarrow C_nH_{2n+1}COONa + HCl.$$

The soaps are in all probability not produced during emulsification by hydrolysis of the glycerides but from impurities present in the oils, since olive oil may be prepared in sufficient purity as not to be affected by the addition of caustic soda the following figures being obtained by Donnan (*Zeit. Phys. Chem.* XXXI. 42, 1899) for the drop numbers of purified and ordinary olive oil in water and caustic soda.

	Drop number in	
	H_2O	N/1000 NaOH
Ordinary ...	58	331
Purified ...	58	58

10. The ageing of emulsions.

By means of mechanical dispersion emulsions may readily be prepared; these however are unstable and on standing the emulsion may break and separate almost completely into the two phases. Instability of emulsions prepared with emulsifying agents such as saponin and protein matter may be ascribed to changes occurring in the protective film such as the irreversible coagulation noted by Ramsden (*loc. cit.*), the film thus becomes brittle and eventually cracks leading to a separation of the emulsified phase. The cracking of emulsions stabilised with soaps on prolonged standing can be attributed to the gradual transformation of the dense soap film at the interface into curds as noted by McBain. In some cases however the protective film appears to become more resistant with age and the apparent stability of the emulsion increases instead of decreasing on standing. Such is the

case with gelatine (Nugent, *Trans. Farad. Soc.* XVII. 703, 1922) where the gelatine film apparently gets thicker on standing.

Nugent noted that caustic soda broke a benzene water emulsion stabilised with gelatine, and that the breaking was preceded by an inhibition period which increased with the age of the emulsion as instanced by the following figures.

Age of emulsion 0·4 % gelatine (hours)	Inhibition period on treatment with 0·5 N.NaOH (minutes)
0	0
2	35
6	45
12	55
24	60
48	70
72	75

Nugent assumes that the gelatine film increases in thickness with age and that the caustic soda strips the film layer by layer. The inhibition period is thus a measure of the thickness of the gelatine layer which evidently on this view increases with age. After 72 hours ageing the inhibition period was found to be constant at 75 minutes, the adsorbed gelatine film now being in true equilibrium with the gelatine in solution, this limiting inhibition period varies with the gelatine content of the emulsion as indicated in the following table.

Gelatine concentration %	Limiting inhibition period (minutes)
0·10	0
0·12	5
0·15	15
0·20	25
0·40	75

The mechanism of the breaking of the protected gelatine emulsion with soda is by no means clear. On the assumption that the gelatinate ion exerts but little stabilising action on the emulsion

by reason both of its solubility and its negative charge we may regard the reaction as a simple diffusion reaction of hydroxyl ions with the gelatine surface,

$$\text{gelatine} + \text{NaOH} \rightleftarrows \text{Na } \textit{gelatinate} + \text{H}_2\text{O},$$

thus being a reaction of zero order whence

$$\frac{dx}{dt} = k \quad \text{or} \quad x = kt.$$

The thickness of the film removed is thus directly proportional to time of inhibition, a conclusion confirmed by the figures given above. It is however somewhat singular that the adsorbed gelatine film should acquire a thickness which is directly proportional to the bulk concentration. Iso-electric gelatine is however but sparingly soluble in water and although the first layer of gelatine may be produced by adsorption subsequent layers may result as a process of removal of supersaturation by condensation on these layers.

CHAPTER V

THE GAS-SOLID INTERFACE

1. Adsorption.

The property possessed by charcoal of absorbing unpleasant smelling gases from the atmosphere has been put to extensive use from the earliest times.

Whilst charcoal possesses this property to a marked extent similar phenomena are to be noted at all solid surfaces. A gas brought into contact with a solid surface will be adsorbed into the surface to an extent which is dependent on several factors, the nature of the gas and solid, the partial pressure of the gas and the characteristic structure of the exposed surface. This phenomenon of adsorption is, however, frequently complicated by solution of the gas in the solid to form solid solutions or compounds with the solid. The term 'sorption has been proposed by McBain to include the two phenomena of absorption and adsorption. Our attention will be limited to the characteristics of adsorption.

2. The surface energy of solids.

Crystals.

In order to break the regular space lattice of a crystal a certain amount of energy must be expended, leading to ultimate disintegration to a gas when the energy expenditure is equal to the latent heat of sublimation. The cleavage of a crystal is accompanied by an increase in the surface area and a slight cooling of the crystal surface, and if the work required to separate a crystal of unit cross-section be u the relationship between the change in the total surface energy u and the free surface energy σ is given by the Gibbs-Helmholtz equation

$$\sigma - u = T\frac{d\sigma}{dT}.$$

The fact that the surface atoms in the plane of a crystal lattice surface possess the power of cohesion can also be demonstrated readily by such examples where clean pieces of platinum can be welded together, the joining of optically smooth glass surfaces and

the virtual coalescence of clean sheet mica under slight pressure. The cohesive power of the surface atoms of one cleavage plane of a crystal face is not limited to the atoms in the other cleavage face but may be exerted on substances entirely dissimilar to the crystal in composition. Atoms in a crystal may in fact be regarded as surrounded by a field of force, and although there is but little residual attraction within the crystal, where each atom is situated symmetrically as regards the electrical forces of cohesion, the unsaturated character or the intensity of this field assumes large values in the space in juxtaposition to the crystal surface.

The surface of a crystal is thus chemically unsaturated and the existence of a definite surface energy is due to the fact that the surface is unsaturated. Since the surface of a crystal consists of a regular lattice of orderly distributed atoms or ions the surface adhesional forces may be regarded as being distributed over the centres of these atoms (Haber, *J.C.S.I.* xxxiii. 50; *Zeit. f. Elektrochem.* xx. 521, 1914) although in all probability these points represent maxima in a continuous field.

The existence of a surface energy affects both the growth and stability of crystals in equilibrium with their vapour or their saturated solutions. In the growth of crystals in solution we note not only additional proofs for the existence of a surface energy of solids but that crystals develop those facets such that the interfacial surface energy will, for equal values of the forces of crystallisation, become a minimum. Similar considerations apply to crystals in contact with their vapour, the growth of the surface in which the packing of the atoms or ions produces a minimum value of the surface energy will be favoured, although such free development is frequently modified by such factors as thermal conductivity and diffusion playing a part in limiting the rate of crystal growth.

The problem of the variation in the surface energies of various crystal facets can be attacked from several points of view. Bravais first noted that those planes of a crystal which were most densely packed and were also separated most distantly from the neighbouring parallel plane were those which appeared most frequently in crystals; he noted also that a closely packed surface was usually associated with a wide interplanar distance and vice versa. Later Willard Gibbs indicated that the most stable planes on a growing crystal were those possessing the least interfacial surface energy.

We thus arrive at a general inference that close packing and a wide interplanar spacing lowers the free energy of the surface. Valeton (*Phys. Rev.* XXI. 106, 1920), Niggli (*Zeit. f. anorg. und angew. Chem.* CX. 55, 1920) and Tertsch (*Zeit. f. anorg. Chem.* CXXXVI. 205, 1924) have attempted to correlate the rate of growth of a crystal face with the interplanar spacing. Thus in a face centred cubic crystal of the rock salt type the interplanar spacing for the 100 : 110 : 111 planes are in the respective ratios $\frac{1}{2}:\frac{\sqrt{2}}{4}:\frac{\sqrt{3}}{3}$, whilst the velocities of growth of the three planes are in the ratio $1:\sqrt{2}:\sqrt{3}$. The 111 plane growing most rapidly possesses the maximum adhesional surface energy and is thus the least stable, the 100 planes being those which possess the least surface energy and thus appear most frequently. Evidently the surface energies, and thus the growth rates are not dependent solely on the interplanar distances, but we must ascribe different valencies or adsorptive powers to the planes themselves.

Tertsch assumes that these stand in the ratio

$$100:110:111::1:2:3,$$

thus giving rise to velocities of growth

$$\tfrac{1}{2}\times 1:\frac{\sqrt{2}}{4}\times 2:\frac{\sqrt{3}}{3}\times 3$$

or $1:\sqrt{2}:\sqrt{3}$, the observed velocities.

Between the alternate $Na^{\cdot}$ and Cl' planes, although the probability of attachment of a Cl' to a $Na^{\cdot}$ plane is twice as great as its probability of attachment to a mixed plane containing both $Na^{\cdot}$ and Cl', in building up several layers the mean probability of growth for such surfaces will be identical with that of a mixed plane.

As justification for this somewhat arbitrary assignment of different degrees of unsaturation or valencies of the ions or atoms in the various planes we may note that any ion in the interior of a face centred cubic crystal may be regarded as the centre of a shell containing six groups of opposite sign round it. An ion in the 100 plane has only five groups of opposite sign round it and requires one more to complete the six which may be regarded as its coordination number, whilst ions in the 110 and 111 planes require two and three ions respectively to complete their sets.

Again we may note that the density of surface packing of atoms

or ions in the various planes of a crystal are in the inverse ratio to the interplanar distance and consequently instead of assuming an increase in attractive power varying as the interplanar distance we may assume that the attractive power falls off as the density of packing of the atoms on the surface increases.

In a face centred cubic crystal of atomic volume V the packing density is as follows (Langmuir, *J.A.C.S.* XXXVIII. 2748, 1916).

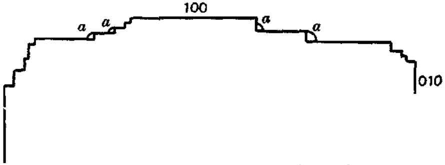
Face	No. per sq. cm.
100	$5{\cdot}56 \times 10^{15}\ V^{-\frac{2}{3}}$
110	$4{\cdot}02 \times 10^{15}\ V^{-\frac{2}{3}}$
111	$6{\cdot}57 \times 10^{15}\ V^{-\frac{2}{3}}$

We have noted however that neither the interplanar spacing or packing density of the planes is a sufficient criterion of stability, for, in rock salt, copper and silver the more open 100 is the most stable facet whilst in gold and platinum the more closely packed 111 planes are the most stable.

To explain these differences we must assume a different surface valency for copper and silver to that for platinum and gold. The simplest assumption to make is that the copper and silver possess a variable valency on each face as assumed for rock salt; whilst the metals forming stable octahedra are those in which a surface atom possesses the same valency irrespective of its position on the crystal surface; the most closely packed surface would then be most stable giving growth rates of $\frac{1}{2} : \frac{\sqrt{2}}{4} : \frac{\sqrt{3}}{3}$. Tertsch (*loc. cit.*) makes the somewhat arbitrary assumption that for these metals the surface valencies vary in the order $100 : 110 : 111 :: 4 : 5 : 3$ giving mean velocities of growth of $2 : 1{\cdot}767 : 1{\cdot}732$.

Not only must we consider the crystal facets themselves from this point of view as differentiated in their respective surface energies but if we consider the corners and edges common to two crystal surfaces we note again that the cohesion of atoms so situated in respect to the mother crystal is far weaker than that for atoms actually in one of the surfaces and we should anticipate that the adhesional energy of such atoms, or the external field, will be greater for these edges and corners than for the planes. A crystal

undergoing a process of growth or solution will be found to possess a step-like structure. Atoms at the corners of the individual steps



$(a\ a)$ are more reactive than atoms in the planes themselves. Thus simple crystals undergoing evaporation or solution will develop the more complicated facets and adsorption on crystals will tend to be greatest on the edges and corners.

The surface energies of simple crystals have been examined from the point of view of the lattice energy of heteropolar compounds by Born (*Atomtheorie des festen Zustands*, 2nd ed. 1923), and by Jones and Taylor (*Proc. Roy. Soc.* A, CII. 496, 1925). The following are typical of the data obtained:

Salt	Plane	σ dynes per cm. Jones and Taylor	σ dynes per cm. Born	$\sigma_{obs.}$ dynes per cm. molten salt
KCl	100	76·6	107·2	69·3
	011	260		
NaCl	100	96	150·2	66·5
	011	350		

Similar computations have been made for the edge energies of such cubic crystals. Jones and Taylor (*loc. cit.*) give the following values:

Salt	Edge energy
NaF	5·13
KF	3·95
NaCl	3·97
KCl	3·06

3. Agglomerates.

The rapid condensation of a vapour to a solid at low temperatures or the drying of a hydrated oxide results in the formation of an agglomerate of atoms or molecules (Langmuir, *Phys. Rev.* VIII. 149, 1916) which, if possessed of sufficient mobility after condensation,

will arrange themselves in crystals possessing a minimum of surface and lattice energy. The mobility of the atoms or molecules is provided by the kinetic energy of thermal agitation and at low temperatures such an agglomerate will be relatively stable. The agglomerate will as we have noted above possess a more intense surface field of force and a greater free surface energy than a crystal. It will be more highly unsaturated (Küster, *Lehrbuch d. allg. Physik*, p. 189, 1916; Pawlow, *Zeit. Phys. Chem.* LXVIII. 316, 1920), exert a higher vapour pressure than the crystalline forms, and exhibit greater powers of adsorption. Substances capable of crystallising in two or more allotropic modifications will likewise possess at all temperatures with the exception of the transition temperatures different surface energies and will consequently exhibit differences in adsorptive powers although smaller in magnitude than in the case considered.

On elevation of the temperature unstable allotropes become converted more rapidly than at low temperatures into the stable modification and tbe increased mobility of atoms at high temperatures produces a similar modification in the rapidly cooled conglomerates or amorphorus substances; this conversion into the crystalline accompanied by a grain growth or a conversion of the microcrystalline into the macrocrystalline state is termed sintering: the preliminary stage in annealing.

On sintering the surface activity progressively becomes less as is indicated by the following data on the adsorption of hydrogen by copper and nickel obtained by Beebe and Taylor (*J.A.C.S.* XLVI. 43, 1924).

	Adsorption at 0° and 760 mm. in c.c. per gm.
A. Active copper	3·70
B. Do. heated at 450° C. for 1·5 hours ...	1·15
A′. Active nickel	35
B′. Do. heated at 400° C. for 4 hours ...	16

Unfortunately these data do not permit of calculation of the change in adsorption per sq. cm. caused by the gradual readjustment of the atomic positions into the stable configurations, since during the process of sintering the superficial surface undergoes contraction as well as a modification in the structure. Some measure

of the cohesive power of the various metals may he obtained from an examination of their sintering temperatures (Smith, *J.C.S.* CXXIII. 2088, 1923), the temperature at which the thermal agitation of the molecules is sufficient to permit of a measurable transition rate of the unstable amorphous material into the more stable crystalline modification. Smith obtained the following values:

Metal	Sintering temperature °C.
Pt. black ...	500
Pd. black...	600
Ppt. Pt ...	750
Ppt. Ni ...	700
Ppt. Co ...	200
Red. Co ...	500
Au ...	250
Ag ...	180
Ppt. Cu ...	250
Red. Cu ...	400

The surface oxidation of a metal such as copper is accompanied by the growth of an oxide layer, the thickness of which may be measured by the method of colour interference when due allowance is made for the refractive index of the oxide formed, or by the decrease in electrical resistance of a thin wire or tube of the metal as oxidation ensues. Investigations have been made on the rate of such oxidations by Tammann (*Zeit. f. anorg. Chem.* CXI. 78; CXXIII. 196; CXXIV. 196), Hinshelwood (*Proc. Roy. Soc.* A, CII. 318), Palmer (*Proc. Roy. Soc.* A, CIII. 444) and Dunn (unpublished, see also: Pilling and Bedworth, *Jour. Inst. Metals*, XXIX. 529, 1923). It is found that the rate of increase in thickness of the oxide film (x) obeys under ideal conditions the ordinary diffusion law or

$$x = kt^2.$$

A preliminary period of rapid oxidation may be eliminated by obtaining smooth surfaces of metal. Of greater interest is the fact that the rate of oxidation falls off in a very characteristic way as the film gets thicker; this fall in rate commences at an earlier stage at high temperatures. Dunn has shown that this is due to a sintering of the oxide film. A newly formed skin of copper oxide is more permeable to oxygen than one maintained at a high temperature

for a short time. It would appear that the copper oxide first formed must be regarded as a smectic layer of copper oxide molecules which only sinter to the crystalline structure of copper oxide on annealing. If such a freshly formed film of copper oxide he reduced at low temperatures back to metallic copper the metal formed is a pseudomorph of the copper oxide and has a much more open packing than the original copper; it is thus more readily oxidised and more catalytically active. Many oxidations and reductions may thus reduce a coherent crystalline metal to a highly active state consisting of irregular orientated strings of copper molecules with relatively wide intermolecular distances.

If a high degree of dispersion on a support material be attained not only will there be an extension of the gas-solid interface but the relative area of the irregular or loosely packed and catalytically active surface will be augmented. The high catalytic activity of metals deposited as mirrors on glass (Hinshelwood, Hartley and Topley, *Proc. Roy. Soc.* A, C. 525, 1922) or on silica gel and the protected catalysts utilising gelatine, gum arabic or lysalbinic acid is due to the artificial stabilisation of these reactive patches. Thus "activation" by alternate oxidation and reduction involves two processes, the extension of the gas-solid interfacial area and the opening of the crystal lattice. If the oxide formed undergoes a sintering process becoming less permeable to oxygen the rate of oxidation of the underlying metal falls off more rapidly than that given by the ideal diffusion equation and approaches the rate given by the empyric logarithmic equation of Tammann

$$t = ae^{bx} - a,$$

where a and b are constants.

A similar departure from the diffusion law to the logarithmic is likewise to be noted when the oxide formed is not of uniform composition but consists of a solid solution of two oxides such as obtains in the case of iron.

4. Phase discontinuities.

Investigations on the adsorption of gases, on the rates of catalytic processes (see Rideal and Taylor, *Catalysis in Theory and Practice*) and on the dissociation of crystalline solids such as hydrates or carbonates have revealed another interesting phenomenon.

We have noted how the free surface energy of a solid surface may be affected by the atomic or ionic configuration in the surface, the individual facets, corners, edges and unstable agglomerates all possessing different values. It would appear from these investigations that the adsorptive power of an atom may be affected not only by juxtaposition of atoms of the same material around it in different configurations and at different distances but also by the juxtaposition of atoms of different materials. Two such cases of "promoter" action may be distinguished, one in which the extraneous or foreign material is incorporated in the solid and the other where the adsorption of two gases by a chemically uniform solid surface affects the strength of union of the gases to the solid.

Faraday noticed that a crystal of a hydrated salt placed in a desiccator did not lose water unless a discontinuity in the surface of the crystal was produced by a scratch, efflorescence proceeding autocatalytically at the ever increasing boundary between dehydrated and hydrated salt. In a similar manner it has been found that the reduction of copper oxide proceeds from a nucleus of copper increasing in rate as the length of the superficial interface between oxide and metal increases. Again Langmuir (*loc. cit.*) has shown that when equilibrium is established in the system $CaCO_3 . CaO . CO_2$ it is extremely probable that the decomposition of the calcium carbonate and the carbonation of the oxide proceeds only at the interface between the chalk and the lime. The union between carbon monoxide and copper is profoundly modified by the juxtaposition of palladium to the copper, whilst a similar effect is noted in the juxtaposition of oxides of the alkaline earths to nickel, the effects of these addition agents being noted by a marked alteration in the rates of catalysis and in the selective adsorption of gases at such "promoted" surfaces.

Somewhat similar in character is the effect of adding an extraneous gas. Thus it has been found (Catalysis, *loc. cit.*) that the rate of reaction between gaseous hydrogen and liquid sulphur is greatly increased by the addition of oxygen. The oxygen is adsorbed as well as the hydrogen and may indeed if present in large quantities displace this gas entirely from the surface. The rate of reaction between hydrogen and sulphur is a maximum apparently when the surface is covered with equal quantities of the adsorbed gases.

5. Porous materials.

In the case of porous materials the pores or capillaries of the solid offer by no means a negligible resistance to the flow of the gas and in consequence penetration may proceed for long periods of time before equilibrium is attained. During this period 'sorption may likewise occur and thus data on the true surface adsorption are liable to be untrustworthy. Charcoal possesses a large specific surface and has been largely employed for the measurement of the adsorption of gases. It is in reality extremely unsuitable for the purpose, for the value of the property of a high specific surface is completely discounted for two reasons, firstly on account of the minuteness of the micropores in the material resulting in a long hysteresis before true adsorption equilibrium is obtained, and secondly, charcoal is in itself extremely variable in composition. Thus charcoals may readily be prepared, their apparent densities varying from $\rho = 1{\cdot}2$ to $\rho = 2{\cdot}26$. It is almost impossible to prepare ash free charcoal, whilst in addition the presence of the gases hydrogen, oxygen and nitrogen present in chemically combined forms is almost unavoidable.

If condensation of liquid in the micropores of charcoal when brought into contact with a vapour should occur the equilibrium vapour pressure above these constricted liquid filled capillaries will be much less than above a plane surface of liquid (see Chap. IX). Under these conditions the liquid filling the pores will be included in the amount of vapour adsorbed by the charcoal and give an erroneous impression as to the true extent of adsorption. At the same time for actual condensation to occur it is necessary that a mobile free surface of liquid should first be formed at some point in the capillary, in order that the surface forces of the liquid may promote further condensation. The primary formation of a layer more than one molecule thick is thus an essential preliminary to the process of capillary condensation.

6. The adsorption isotherm.

Accurate data on the adsorption of gases by various charcoals have been collected by numerous investigators notably Hempel and Vater (*Zeit. Elektrochem.* 724, 1912), Travers (*Proc. Roy. Soc.* A, LXXVIII. 9, 1906), Homfray (*Zeit. Phys. Chem.* LXXIV. 139, 687, 1910), Titoff

(*ibid.* 174, 641, 1910), Geddes (*Ann. der Phys.* XXIX. 797, 1909), Richardson (*J.A.C.S.* XXXVIII. 1828, 1917) and others.

Many attempts have been made to express the curves relating the amount adsorbed per gm. of charcoal to the gas pressure in simple mathematical form, notably by Freundlich, Arrhenius, Williams and Langmuir.

It is found that at any rate within limits a fair agreement is obtained between the experimental data and a curve by means of an empyric equation, the adsorption isotherm of Freundlich.

This equation, is generally expressed in the form

$$\frac{x}{m} = ap^{\frac{1}{n}},$$

where x is the amount of gas adsorbed per m gms. of charcoal under a gas pressure p, and a and n are arbitrary constants.

The value of a is dependent on the units employed for measurement, whilst n is a characteristic not only of the adsorbing agent but also of the adsorbate. Thus at 20° C. the approximate values of $\frac{1}{n}$ for a few easily liquefiable gases are as follows:

Gas	$\frac{1}{n}$ for charcoal	$\frac{1}{n}$ for glass
CO_2 ...	0·394	0·66
NH_3 ...	0·437	0·53
SO_2 ...	0·324	0·28
$CHCl_3$...	0·122	—
N_2O ...	—	0·49

The two arbitrary constants likewise vary with the temperature and we note as significant not only that $1/n$ approaches unity as the temperature is elevated but also it is in reality not a constant over a wide range since it increases as the gas pressure is reduced.

Chappius (*Wied. Ann.* XIX. 29, 1883) obtained a value of $\frac{1}{n} = 0{\cdot}84$ for the adsorption of ammonia by charcoal at pressures between 3–5 mm., whilst from Travers' (*loc. cit.*) data on the adsorption of carbon dioxide by charcoal the following variations may be noted:

Temp. °C.	a	$\frac{1}{n}$
−78	14·290	0·133
0	2·960	0·333
35	1·236	0·461
61	0·721	0·479
100	0·324	0·518

The isotherm of Freundlich possesses two variables n and a which permit of a great latitude in the adjustment of a curve to suit the experimental data. If we combine the equation of Freundlich, $\frac{x}{m} = ap^{\frac{1}{n}}$, with that of Gibbs

$$\Gamma = -\frac{d\sigma}{d\mu} = -\frac{p}{RT}\frac{d\sigma}{dp},$$

in which we replace Γ by x, the amount adsorbed per sq. cm., we obtain

$$-\frac{p}{RT}\frac{d\sigma}{dp} = ap^{\frac{1}{n}},$$

or

$$-d\sigma = aRTp^{\frac{1}{n}-1}\,dp.$$

On the assumption that a is independent of the pressure we obtain

$$-\sigma = naRTp^{\frac{1}{n}} + c,$$

when $p = 0$, $\sigma = \sigma_0$, whence

$$c = -\sigma_0, \quad \sigma_0 - \sigma = F = naRTp^{\frac{1}{n}}.$$

Accurate plotting of the experimental data in the logarithmic form

$$n \log \frac{x}{m} = nA + \log p$$

reveals the fact that in no case does a linear relationship obtain, provided that the adsorption is determined over a sufficiently extensive range of pressures. This departure from the Freundlich equation is most marked at extremely low pressures and not inconsiderable at high pressures. Although the Freundlich isotherm possesses two variables permitting of a considerable latitude

in adjustment yet the data almost always reveal an increasing value for $\frac{1}{n}$ as the pressure is reduced.

It is evident that according to this equation there is no saturation maximum for a definite area of adsorbing surface. Indefinite increase of the pressure produces indefinitely large adsorption. The experimental data, especially those of Schmidt (*Zeit. Phys. Chem.* LXXIV. 689, 1910), Langmuir (*loc. cit.*), Taylor and Rideal (*Catalysis in Theory and Practice*) indicate in a perfectly definite manner that in many cases an adsorption maximum or surface saturation is obtained. Arrhenius (*Medd. Nobel Inst.* II. 7, 1911) was the first to introduce the concept of a definite saturation value (s) which varied with the nature of the adsorbing agent and with the adsorbate. On the hypothesis that the amount taken up for a small alteration of the pressure depended on the relative extent of surface saturation already obtaining Arrhenius showed that the p, x curves could be expressed in the form

$$k\frac{dx}{dp} = \frac{s-x}{x},$$

or

$$\log_{10}\frac{s}{s-x} = 0{\cdot}4343\frac{x}{s} - \frac{0{\cdot}4343}{ks}p.$$

The equation is thus superior to that of Freundlich in that the existence of a surface saturation is realised as well as a physical significance is given to one of the constants.

The following values represent the surface saturation constants s for charcoal in c.c. at N.T.P. per gm. together with the a constant of the Van der Waals' equation for the respective gases.

Gas	s in c.c. at N.T.P. per gm.	$a \times 10^3$
He ...	0·227	0·42
Ar ...	1·67	2·59
N_2 ...	2·35	2·68
O_2 ...	2·50	2·69
CO ...	3·20	2·80
CH_4 ...	9·4	3·67
CO_2 ...	30·4	7·01
NH_3 ...	71	8·08
C_2H_4 ...	41	8·83

Although there is some experimental justification for the conception of a saturation concentration yet this equation containing but one variable was found by Schmidt to conform to the experimental results but very indifferently. Schmidt (*Zeit. Phys Chem.* LXXVIII. 667, 1912) made the additional hypothesis that the adsorption coefficient k decreases in magnitude with the amount of gas adsorbed in an exponential manner, or

$$k = k_0 e^{-Ax},$$

where A is a constant, obtaining thus the equation

$$\frac{dx}{dp} = k_0 (s - x) e^{-Ax} \text{ or } ln \frac{s}{s - x} - Ax = Kp,$$

an equation somewhat similar in form to that proposed by Arrhenius. That these equations do not, in actuality, express the adsorption isotherm over very wide ranges of pressure can be seen from the following values of k calculated with the aid of the Arrhenius equation from the experimental data of Titoff and Homfray:

CO_2 on charcoal at 0° C.		C_2H_4 on charcoal at 0° C.	
P_1	k	P_1	k
0·05	24·9	7·00	12·3
0·32	159·0	4·00	13·2
1·09	89·0	2·28	11·3
2·54	60·5	1·70	11·2
8·30	52·0	0·87	11·6
17·35	48·9	0·54	10·4
31·59	52·7	0·15	11·3
45·72	56·0		
58·91	58·9		
70·32	61·6		
75·51	62·2		

Schmidt has proposed, without theoretical basis however, a more general equation of the type

$$\left(\frac{a - x}{v}\right) S = Ke^{\frac{A(s-x)}{s}} x,$$

where $\frac{a - x}{v}$ is the concentration in the vapour phase in equilibrium with a surface on which x gm. mols. are adsorbed. The agreement is

somewhat better but the wide variations in the observed and calculated values of the constant K are certainly outside the range of experimental error.

Williams (*Proc. Roy. Soc. Edinburgh*, 287, 1919) assuming that the surface concentration was always proportional to the pressure or $x = ap$ obtained an equation $\log \frac{x}{p} = k_0 - k_1 x$, where k_0 and k_1 are functions of the temperature only. A close agreement was found between his equation and the data obtained on the adsorption of sulphur dioxide on charcoal. Langmuir (*Phys. Rev.* VIII. 149, 1916; *Proc. Nat. Acad. Sci.* III. 141, 1917; *J.A.C.S.* XL. 1360, 1918) as a result of a series of experiments on the adsorption of gases on the surfaces of mica and platinum at extremely low pressures also arrived at the conclusion that the Freundlich isotherm does not represent the p, x curve with any degree of accuracy. His interpretation of the mechanism of adsorption as a dynamic equilibrium between the process of condensation and of evaporation has been one of the most fruitful suggestions in the study of heterogeneous catalytic reactions.

The surface of a solid may be regarded as a space lattice work of the elementary atoms, each elementary vacant space above each atom being the possible home of a condensed gas atom or molecule. As we shall note occasionally the adsorbed gas molecule may occupy not one but two or three and in rare cases four of these elementary spaces.

The union between the adsorbed molecule and the adsorbate is thus similar in character to the valency forces holding atoms together in a molecule and univalent, divalent or trivalent surface combinations may thus be formed.

If a gas molecule strikes an empty space on the elementary crystalline space lattice it condenses and is held for a period of time (τ) on the surface before it evaporates. This period of time between condensation and evaporation or the mean life of the molecule on the surface may vary from a small fraction of a second to an almost indefinite period. In those cases where the strength of union between adsorbate and adsorbing agent is weak and where the adsorbed molecule readily receives sufficient kinetic energy from shocks, provided by bombarding gas molecules and pulses from the solid adsorbate, to equal the latent heat of evaporation,

the mean length of life is smallest or the probability of escape is greatest.

By experiment Langmuir showed that the reflexion of a gas striking a solid, i.e. the number of molecules which strike a surface and rebound without condensation, is generally very small, the coefficient of accommodation a being nearly unity.

On the assumption that at equilibrium the rate of condensation of a gas on an adsorbing surface is equal to the rate of evaporation from the covered portion of the surface an adsorption isotherm can be derived.

The rate of effusion of a gas from an orifice has been shown by Herz and Knudsen to be given by the equation

$$\mu = 43{\cdot}75 \times 10^{-6} \frac{p}{\sqrt{MT}},$$

where

μ gm. mols. effuse per sq. cm. of orifice per second,
p is the gas pressure in bars (10^6 bars $= 1$ atmosphere),
M is the molecular weight of the gas,
T the temperature in ° K.

Since the coefficient of accommodation at most surfaces is almost unity a gas striking a surface may be regarded as effusing into a vacuum.

If the surface be partly covered with the gas the impinging molecules will strike and adhere to the vacant portions.

At equilibrium a fraction θ' of the surface will be covered with adsorbed gas and a fraction θ will still be bare.

We thus obtain $\theta + \theta' = 1.$

The rate of condensation of the gas on the uncovered portions of the surface will be $\alpha\mu\theta$, whilst the rate of evaporation from the covered area will be $\nu\theta'$, where ν is the rate of evaporation from unit area. At equilibrium the rate of condensation and evaporation will be equal or

$$\nu\theta' = \alpha\mu\theta,$$

$$\therefore \theta' = \frac{\alpha\mu}{\nu + \alpha\mu}.$$

If we put $\frac{\alpha}{\nu} = t$ then $\theta' = \frac{t\mu}{1 + t\mu}.$

If x gm. mols. are adsorbed per unit area then $\theta' = \frac{N}{N_1} x$, where N is the number of elementary spaces per sq. cm. of surface and N_1 Avogadro's number ($6{\cdot}065 \times 10^{23}$ molecules per gm. mol.).

Hence $$x = \frac{N_1}{N} \frac{t\mu}{(1+t\mu)} = \frac{abp}{1+ap},$$

since $\mu = kp$, which is Langmuir's equation for the adsorption isotherm, where a and b are constants, a being proportional to the length of life of the adsorbed molecule on the surface. At very low pressures where ap is small compared with unity we obtain

$$x = abp,$$

or the amount adsorbed is proportional to the gas pressure. At very high pressures we obtain $x = b$ or a definite saturation maximum is obtained.

It will be noted that on Langmuir's hypothesis the surface becomes saturated when it is covered with a unimolecular thickness of adsorbed gas. By measuring the adsorption of gases on the surface of mica and of platinum Langmuir showed that with the exception of carbon monoxide, gases such as oxygen, nitrogen and methane apparently when adsorbed to a saturation value covered the surface with a unimolecular thickness of gas.

The data for carbon monoxide adsorbed on platinum were found not to obey this equation but to conform more closely to the equation of the type

$$x = b' + \frac{abp}{1+ap}.$$

It may be suggested that carbon monoxide is adsorbed extremely tenaciously by platinum and that b' represents a unimolecular film covering the platinum on the top of which a second film may be built up.

7. On the existence of multimolecular films.

It has been noted that the investigations of Freundlich lead one to the conception of an adsorbed atmosphere of gas consisting of a dense gas film, the density falling off presumably in an exponential manner with the distance from the adsorbing surface. This point of view* was adopted firstly by Faraday and at a later date by

Bodenstein to interpret the mechanism of heterogeneous catalytic actions. Langmuir rejected the hypothesis of a film exceeding one molecule in thickness, but his hypothesis is in reality only confirmed for gases at low pressures and far removed from their critical points. Many measurements have been made on the amounts of gases adsorbed on definite areas of substances such as quartz, glass, wool, powdered glass and the like, notably by Mülfarth (*Ann. der Phys.* III. 328, 1900), Briggs (*Jour. Phys. Chem.* IX. 617, 1905), Katz (*Proc. Amst. Acad.* XV. 445, 1912), Langmuir (*Trans. Amer. Inst. Elect. Eng.* XXXII. 1921) and Evans and George (*Proc. Roy. Soc.* A, CIII. 191, 1923) in which the total quantity of gas adsorbed was found to exceed the amount calculable on the assumption of the existence of a unimolecular film. Some of these data for the film thicknesses obtained are tabulated below:

Powdered glass	Molecular film thickness at 0° and 121 mm.
SO_2 ...	32·1
NH_3 ...	39·9
N_2O ...	4·5
C_2H_4 ...	3·5
H_2O ...	5·6
CO_2 ...	4·8—5·9
N_2 ...	1·0

Similar high values for the thickness of the adsorption film have been found for the adsorption of liquids by materials such as sand by Pettijohn (*J.A.C.S.* XLI. 477, 1919), glass, wool (see *Phil. Mag.* VI. 517, 1903) and by Imorhi for metals (*Wied. Ann.* XXXI. 100, 1887). On the other hand Carver (*J.A.C.S.* XLV. 63, 1923) obtained but a unimolecular film for toluene on a glass surface after prolonged outgassing of the glass over, however, a very restricted range of pressures. In those cases where the unimolecular character of the film is exceeded alternative hypotheses may be advanced in explanation. We may with Langmuir adopt the view that these cases are really exceptional, since these particular gases may actually go into solution, and the solids examined may be full of cracks and fissures of submicroscopic dimensions, thus leading to a very considerable underestimation of the available surface. Another factor

which has to be considered is one based upon the results obtained from a study of the effects of poisons on catalytic surfaces (see Rideal and Taylor, *Catalysis in Theory and Practice*) is that all portions of the surface are not equally effective as an adsorbing agent. We have already had occasion to note that an apparently uniform homogeneous surface will in reality be extremely unhomogeneous in respect to its adsorbing power, the free atoms, the corners and edges of individual crystals and the various crystal faces all differing in the magnitudes of their surface energies. A gas but feebly adsorbed such as argon will adhere only to those portions of the surface where the adsorbing forces are strong, whilst carbon monoxide which is relatively strongly adsorbed will adhere to all parts of the surface. Thus the saturation value of a gas or the availability of a surface will vary in accordance with the system chosen.

We find for example that the saturation capacities of a metal such as copper varies with the nature of the gas. For ethylene and hydrogen the ratio of the saturation capacities at 0° C. on active reduced copper is 2·3 : 1, for copper which has been sintered at 450° C. the ratio is found to be 5·9 : 1. Whilst the total adsorption per gm. of metal has fallen only some 20 °/₀ for ethylene the adsorption for hydrogen has been very seriously diminished. With carbon monoxide, ethylene and hydrogen on copper the ratio of the saturation capacities is of the order 3 : 2·3 : 1. Evidently parts of the copper are accessible to carbon monoxide which do not retain either ethylene or hydrogen. In catalytic investigations a still more marked differentiation in the adsorptive capacities of various parts of the surface must be presumed. Thus in the combination of ethylene and hydrogen on a nickel surface we find that the fraction of the surface area which is catalytically active is of the order of 10^{-4}. There are thus areas of the highly reactive localised patches which can adsorb and cause reaction in these gases, there are other less active areas which can adsorb both gases but fail to bring them into reaction and there exist still less active areas which can adsorb only ethylene but not hydrogen. On analogy with the copper surface it is probable that a small residual area exists on which neither ethylene nor hydrogen is adsorbed at a pressure of 760 mm. and at 0° C. One of the most interesting cases which await examination

from this point of view is the behaviour of crystalline and glassy quartz as a catalyst in the oxidation of carbon monoxide investigated by Bodenstein and Ohlmer (*Zeit. Phys. Chem.* LIII. 175, 1905).

Langmuir has shown that Bodenstein and Ohlmer's results may be interpreted on the assumption that carbon monoxide is strongly adsorbed on the glassy but only feebly on the crystalline material.

If we consider the surface of quartz to be divisible into two areas on which the lengths of life of the carbon monoxide molecule are t_1 and t_2 the amount of gas adsorbed on the total area at a pressure p will evidently be

$$x = \frac{N_0}{N}\left\{\frac{b' t_1 \mu}{1 + t_1 \mu} + \frac{b'' t_2 \mu}{1 + t_2 \mu}\right\},$$

where b' and b'' are constants and

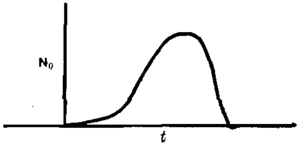
$$\mu = \kappa \frac{p}{\sqrt{MT}}.$$

If t_1 is much larger than t_2 the saturation value b' of the very active area will be attained before the second term becomes at all large and there will be an apparent break in the x, p curve: such a case has been noted by Gustaver (*Koll. Beiheft*, XV. 219, 1921) in the adsorption of picric acid from solution by charcoal.

Again if centres of varying activity exist on the quartz surface we obtain

$$x = \frac{N_0}{N}\int \frac{t\mu \delta b}{1 + t\mu},$$

and a non-linear relationship between x and μ will be obtained.



In an extreme case of random disposition we might further assume that the number of atoms possessing an adsorbing power such that the life of the adsorbate is t will be governed by the laws of probability. The saturation value for a particular t will thus be $b_t \propto N_t$ and $N_\sigma = \kappa t^2 e^{-t^2}$.

Hence we obtain

$$x = \frac{N_0}{N} \int \frac{t\mu \delta b}{1 + t\mu} \quad \text{and} \quad b = \kappa t^3 e^{-t^n},$$

from which the general form of the x, p curve may be obtained.

A differentiation in the activities of surfaces may likewise be witnessed in a variety of chemical and catalytic processes. Thus we find that charcoal will undergo slow autoxidation when exposed to air; it will also catalytically accelerate the oxidation of a number of organic subtances such as oxalic acid. By processes of selective poisoning of the charcoal it can be demonstrated quite readily that the portion of the surface which can accelerate the oxidation of oxalic acid is but a small portion of the surface which is available for say the adsorption of methylene blue and that but a minute fraction of the surface (less than 0·5 $^\circ/_\circ$ for a good sugar charcoal) is capable of undergoing autoxidation.

Vavon and Husson (*C.R.* CLXXV. 277, 1922) have likewise clearly demonstrated the existence of patches of varying activity in platinum black by showing that the progressive addition of a poison such as carbon disulphide will first inhibit the catalytic hydrogenation of substances more difficult to hydrogenate such as acetophenone without appreciably affecting the activity in respect to hydrogenation of nitrobenzene which is readily reduced.

Richardson and Young (*Proc. Roy. Soc.* A, CVII. 377, 1925) in an examination of the thermionic and photoelectric emission from surfaces of sodium and potassium have observed more than one threshold value for the work functions and suggest that in these cases also there are small patches of the surface associated with a low value of the work function.

We have so far discussed two possibilities alternative to the assumption of the existence of multimolecular films and enquiry is necessary to examine how far all existing data can be reconciled to the assumptions either of a capillary surface or a surface variable in accessibility. It must be admitted that these views do not seem adequate to explain all cases of adsorption. Thus in the data presented by Evans and George it is rather singular that the amount of nitrogen adsorbed on glass should be equal to the computed unimolecular film whilst the other easily liquefiable gases exceed this thickness. Langmuir's data on the adsorption of carbon

monoxide by platinum likewise make it appear probable that more than one molecular thickness may be built up. In the case of the adsorption of vapours the evidence for multimolecular films is still more convincing. Carver's values for toluene were restricted to extremely low pressures, between these pressures and the pressure which would be in equilibrium with the bulk liquid toluene a thickening of the film must take place. The pressure difference is too great to presume that the second layer of molecules on the top of the first adsorbed layer will behave like the molecules on the surface of the free liquid. We note again in Iredale's experiments on the adsorption of ethyl acetate vapour on the surface of mercury that after a unimolecular saturated film has been formed the surface tension of the ethyl acetate mercury interface does not drop at once to the value anticipated from the interfacial tensions between surfaces of the two liquids in bulk, a very considerable thickening of the film must occur before the surface of the adsorbed ethyl acetate possesses the properties of a surface of liquid ethyl acetate.

Similar conclusions may be drawn from the experiments of Hardy on lubrication. Hardy has obtained very convincing data in support of the hypothesis that on the adsorption of a vapour such as octyl alcohol by a metal surface, whilst the first layer is held very tenaciously the thickness of the film of vapour condensed on the metal surface which is in equilibrium with the free surface of the liquid is certainly multimolecular in character and those layers forming the secondary film may be squeezed out by application of sufficient pressure.

Examination of the temperature gradients at the surfaces of heated metal in air at high pressures (*ca.* atmospheric) likewise reveals the existence of a thin but multimolecular film in contact with the hot metal.

It must be concluded that although the first layer of adsorbed molecules is held extremely tenaciously and that a large decrease in free energy occurs on the adsorption of a unimolecular layer of gas, a further but smaller decrease in free energy may take place on the further adsorption of gas in the secondary films. We would anticipate that a surface of feeble adsorptive power such as diamond would be almost completely saturated with a unimolecular layer, but active surfaces such as of metals are not completely saturated.

If the adsorbate be a vapour possessing a high natural cohesion, i.e. a large "a" value for the Van der Waals equation of state and the vapour be present at not too low a pressure, multimolecular films may be built up on the primary. Even in the case of gases with a relatively large value of "a" and at sufficiently high pressures multimolecular films may be formed on active adsorbents, e.g. CO on platinum. Gases such as hydrogen and nitrogen probably form only unimolecular films even at very high pressures.

8. The heat of adsorption.

When an adsorbing surface is exposed to a gas or vapour adsorption will take place, being accompanied by the absorption or evolution of heat. Such thermal changes have already been noted in the extension and contraction of surface films of liquids. Although the direct determination of the surface energy of solid surfaces presents many experimental difficulties yet of its existence there is no doubt. On the adsorption of a gas or vapour a diminution in the free surface energy of the system likewise occurs. From the Gibbs-Helmholtz relationship

$$u = \sigma - T\frac{d\sigma}{dT},$$

it is clear that if the heat of adsorption be measured in gm. mols. per square centimetre of surface we obtain the value of $T\frac{d\sigma}{dT}$. Also since $\sigma = \int \frac{Q}{T} dT$ a direct determination of the surface tension of the solid-gas interface is obtainable provided that we can integrate the above expression. This is evidently possible if we can determine the value of T at which $\sigma = 0$. By analogy with the liquid-air surface σ and $\frac{d\sigma}{dT}$ vanish together, so that by means of a series of determinations of the heats of adsorption over a temperature range some valuation of the surface tension of a solid-gas interface might be possible.

There are three isothermal heats of adsorption of gases capable of being defined:

(a) The equilibrium value, where the adsorption proceeds in such a manner that the vapour phase is continually in equilibrium with the adsorbed layer.

(*b*) The heat of adsorption at constant pressure, in which the gas is at constant pressure but not necessarily the equilibrium pressure.

(c) The heat of adsorption at constant volume in which the total volume of the system is kept constant and the gas is adsorbed with a fall in pressure.

The thermodynamical relationship between these heats of adsorption has been developed in an exact form by Williams (*Proc. Roy. Soc. Edin.* XXXVIII. 24, 1918) who has deduced the following values:

(*a*) The isothermal equilibrium heat of adsorption λ_T.

From the Gibbs-Helmholtz equation

$$dU = TdS - dW,$$

we obtain for a solid adsorbent of area A and surface tension σ in equilibrium with a gas at pressure p and temperature T submitted to a small reversible charge where dU and dS are complete differentials

$$dU = -\lambda_T dx - pdV + \sigma dA,$$

$$\lambda_T = -\left(\frac{dU}{dx}\right)_{gT} - p\left(\frac{dV}{dx}\right)_{gT} + \sigma\left(\frac{dA}{dx}\right)_T,$$

where g is the number of gms. of adsorbent adsorbing at p and T

$$= -\left(\frac{dU}{dx}\right)_{gT} + pV - (n-x)p\left(\frac{dV}{dp}\right)\cdot\left(\frac{dp}{dx}\right)_T + \sigma\left(\frac{dA}{dx}\right)_T,$$

where n is the number of mols. of gas in the system. The third term represents the work done by the gaseous phase in expansion and may in general be neglected.

(*b*) The isopiestic isothermal heat of adsorption λ_{pT}

$$\lambda_{pT} = -\left(\frac{dU}{dx}\right)_{gT} + p'V'\left(\frac{dx'}{dx}\right),$$

where $\frac{dx'}{dx}$ is the ratio of the gas entering the adsorption chamber to the gas actually adsorbed, which for low pressures will be approximately unity.

(*c*) The isothermal heat of adsorption at constant volume λ_{vT}

$$\lambda_{vT} = -\left(\frac{dU}{dx}\right)_{gT}.$$

In actual practice the heat effect measured will be $\int_{x_1}^{x_2} \lambda dx$ and no one of the above conditions is rigidly fulfilled.

For gases which may be considered ideal we evidently obtain

$$\lambda_{pT} = \lambda_{vT} + RT.$$

If the area of the adsorbing surface remain constant we obtain

$$\lambda_{pT} = VT\left(\frac{dp}{dT}\right)_x = RT^2\left(\frac{d \log p}{dT}\right)_x,$$

which corresponds to the Clapeyron equation.

The following data indicate the close agreement between the data obtained by Titoff and those calculated with the aid of this equation for the heat of adsorption of ammonia by charcoal at 0° C. λ is calculated and determined in calories per c.c. of ammonia (at N.T.P.) adsorbed. x is measured in c.c. per gm. at N.T.P.

$\log_{10} x$	λ calc.	λ obs.
2·10	·265	·386
2·00	·290	·355
1·80	·319	·360
1·60	·329	·370
1·40	·340	·375
1·20	·340	·388
1·00	(·40)	·410
0·80		·430
0·50		·450

Data for the heats of adsorption of gases on metals are as yet scanty but the following values may be cited.

Adsorbing agent	Gas	Cals. per gm. mol. at 0° C.
Palladium ...	H_2	18,000*
Platinum ...	H_2	13,760*
	CO	35,000*
Nickel ...	H_2	11,340–12,000
Copper ...	H_2	9,500
Nickel ...	C_2H_4	5,845
	C_2H_6	5,004

* Favre, 1894; Langmuir; Rideal, *J.C.S.* CXXI. 309, 1922; Foresti, *Gaz. Chim. Ital.* LIII. 487, 1923, LIV. 132, 1924; Taylor and Burns, *J.A.C.S.* 1923.

Palmer (*Proc. Roy. Soc.* A, CVI. 200, 1924) in investigating the effect of various gases on the sensitiveness of a coherer or loose contact has noted that the potential required to break down the loose contact between platinum, tungsten and carbon films varies with the nature of the gas.

For many gases the potential is quite characteristic and is unaffected by alterations in gas pressure over a wide range. In other cases the potential required increases with the time for which the gases have been in contact with the filament.

On the assumption that the insulating gas films are unimolecular and that the energy of desorption per sq. cm. may be expressed by the equation

$$E = \frac{(K-1)\left(\frac{V^2}{300}\right)^2}{8\pi d} \text{ ergs,}$$

where V is the potential at which breakdown occurs, i.e. desorption of the gas, and $d = 2\sigma$ where σ is the molecular diameter, Palmer has calculated the following values for the energies of desorption.

HEAT OF DESORPTION IN CALORIES PER GM. MOL.

Gas	Tungsten	Platinum	Carbon
O_2 ...	10,800	1,200	—
H_2 ...	166	160	—
CO ...	from 100 for a fresh film to 32,000 max.	750	—
NO ...	950	950	—
NH_3 ...	7,300 max.	—	—
SO_2 ...	8,010	5,340	—
H_2O ...	40,000	—	—
C_2H_6 ...	small	—	5,400
C_2H_4 ...	"	—	2,550
C_2H_2 ...	—	—	4,900
N_2 ...	less than 2	—	—

As yet no conclusive evidence of a variation in the heat of adsorption with the physical characteristics of the metal surface has been presented. We would however anticipate that amorphous or irregular surfaces should adsorb more strongly and consequently

both the affinity of the reaction of adsorption and the heat effect should be larger than for microcrystalline surfaces.

The heat of adsorption of vapours.

Lamb and Coolidge (*J.A.C.S.* XLII. 1146, 1920) have studied the heat of adsorption of a number of easily liquefiable vapours on charcoal. They showed that the heat evolved per gm. of charcoal h was a function of the amount adsorbed expressible in the form $h = ax^b$.

The following values were obtained for a and b with various vapours:

Vapour	a	b
CCl_4 ...	0·893	0·930
$C_2H_5OC_2H_5$	0·917	0·921
CCl_3H ...	0·829	0·935
$HCOOC_2H_5$	0·944	0·907
CS_2	0·752	0·920
CH_3OH ...	0·742	0·938

They also arrived at the following conclusions:

(*a*) The greater the molecular volume the less adsorbable was the substance for a definite pressure and temperature.

(*b*) The greater the number of molecules adsorbed at a given pressure the smaller the heat of adsorption.

(*c*) Assuming the adsorbed gas to be in the liquid state then the net heat of adsorption per c.c. of liquid was found to be identical for all substances examined as indicated by the following data:

Substance	H Heat evolved per gm. mol. for adsorption of 1 c.c. of liquid per 10 gms. of charcoal. Cals.	L Molecular heat of vaporisation. Cals. per gm. mol.	$H-L$ Molecular net heat of adsorption	$\frac{H-L}{(V)}$ Heat of adsorption per c.c. of liquid
CCl_4 ...	16,090	6,900	9,190	85·6
C_2H_5Cl ...	12,330	6,200	6,110	86·4
C_6H_6 ...	15,170	7,810	7,310	85·0

The variation in the heat of adsorption of ammonia by meerschaum has been likewise examined by Chappuis (*Wied. Ann.* XIX. 21, 1883) over an extended range of pressures with the following results:

Pressure cm. Hg	Q cals. per gm. mol.
0	20,500
0 - 0·5	12,700
0·5 - 3·7	11,300
2·9-21	8,970
21 -57	7,600
Heat of liquefaction	5,000

In this case also the heat of liquefaction is approached at high pressures. Although we might anticipate that the very active centres on the adsorbing surface would exhibit a higher heat of adsorption than less active centres and that the former would be covered at low pressures the latter only at high pressures, yet the enormous quantity of vapours adsorbed and the constancy of the heat of wetting for various vapours indicates that we are in all probability dealing with the formation of a secondary film.

We can note for example tbat 1 gm. of charcoal contains 5×10^{22} atoms and that the saturation maximum of ammonia is *ca.* 158 c.c. at N.T.P. or 4×10^{21} atoms; the adsorption maximum of bromine 10 millimols or 6×10^{21} atoms. Still larger quantities of other gases, e.g. SO_2, are adsorbed.

A further insight into the nature of the forces forming the secondary film or multimolecular layers in the adsorption of vapours is provided by the recent experiments of McHaffie and Lenher (*J.C.S.* CXXVII. 1559, 1925) on the adsorption of water vapour by glass and platinum. On the assumption that water vapour may be regarded as behaving as a perfect gas up to pressures of some 40 mm. these investigators have determined the pressure exerted by a limited amount of water vapour in contact with glass and platinum surfaces over a range of temperatures. In all cases the pressures observed within a certain temperature range were less than those anticipated if all the water existed in the vapour state. The deficiency of pressure

observed is ascribed to adsorption of the water vapour, and with a knowledge of the area of adsorbing surface, the molecular thickness and the equilibrium pressures for these thicknesses could be determined. The decrease in free energy accompanying the adsorption of water on the nth layer can readily be calculated from the equation

$$-\Delta F = RT \log \frac{P_n}{P},$$

where P_n is the vapour pressure in equilibrium with a layer of adsorbed water n molecules thick and P the vapour pressure of water at the temperature T.

Two series of determinations of McHaffie and Lenher are given below.

ADSORPTION ON GLASS.

Temp. °K.	P in mm.	Thickness of film in molecules	$-\Delta F$ cals. per gm. mol.
293	16·90	88·5	20·6
298	22·73	51·8	26·1
302	27·54	22·5	52·2
305	29·71	10·5	110·4
308	30·65	5·9	194·8
311	31·44	2·7	282·2
314	31·97	1·4	374·1
317	32·40	0·6	468·2
320	32·80	—	—

ADSORPTION ON PLATINUM.

Temp. °K.	P in mm.	Thickness of film in molecules	$-\Delta F$ cals. per gm. mol.
293·5	18·01	22·30	0
294	18·96	18·40	6·06
295	19·10	12·70	35·50
297	20·32	2·50	57·00
298	20·61	0·28	84·10

9. Molecular orientation in adsorption.

The characteristics of metals in exerting a specific action in adsorption of gases which for the more perfect gases results in the formation of a unimolecular layer and for vapours multimolecular

layers permits us to examine how far the union between adsorbent and adsorbate may be regarded as essentially chemical in character as imagined by Haber and Langmuir (*loc. cit.*) for gas-solid interfaces and by Hardy and Langmuir for liquid-gas interfaces.

From a consideration of the velocity of a number of heterogeneous gas reactions (Rideal and Taylor, *Catalysis in Theory and Practice*) a certain number of conclusions may be drawn in respect to the valency of the adsorbate and the number of elementary spaces on the crystal lattice which the adsorbate occupies or adheres to. If we consider a unimolecular reaction to occur catalytically at a surface, e.g. $X_2 \leftrightarrows 2X$, and that the reactant is but feebly adsorbed by the catalyst, then adopting the previous notation the rate of condensation of the gas on the surface of the catalyst (since the catalyst is almost bare) will be $\alpha\mu$. If the reactant X_2 occupies a fraction θ and each molecule n elementary spaces on the lattice the rate of evaporation of the unchanged product will be $\nu\theta^n$. Provided the chemical reaction occur but slowly we obtain

$$(1) \quad \alpha\mu = \nu\theta^n.$$

If the chemical reaction proceed by the combination and evaporation of molecules from m adjacent spaces the velocity of chemical change will be given by

$$(2) \quad \frac{dx}{dt} = \nu_2\,\theta^m.$$

Hence from (1) and (2)

$$\frac{dx}{dt} = \nu_2\left(\frac{\alpha\mu}{\nu}\right)^{\frac{m}{n}}.$$

The velocity will thus vary as the m/n power of the gas pressure. In the case of the dissociation of hydrogen molecules into atoms at the surface of a hot metal wire Langmuir found $m/n = \frac{1}{2}$, whilst for the recombination of atoms at a surface m/n was found to be 2.

Thus if we insert the values $m = 1$ and $n = 2$ in the first case and $m = 2$, $n = 1$ in the second, so that the hydrogen atom is held on by one elementary space and the hydrogen molecule by two elementary spaces, the conception of a uni- and divalent union is readily realised. In this way a "valency" of two for carbon monoxide, sulphur trioxide and ammonia on platinum; two for the oxygen molecule and one for carbon monoxide on quartz can be established.

Another method of attempting to establish the valency of the adsorbate or the number of elementary spaces occupied by an adsorbed molecule lies in the investigations on the poisoning of catalysts. We find for example (e.g. Maxted, *J.C.S.* cxv. 1050, 1919) that small quantities of sulphur poison, so far as hydrogen adsorption and catalytic hydrogenation are concerned, palladium black. Quantitatively it is found that some four atoms of palladium are poisoned for each atom of sulphur adsorbed. No quantitative data on catalytic activity and the actual adsorption of the poison are forthcoming, although the approximately linear relationship between poison concentration and decrease in catalytic activity has been well established. A more minute investigation of this process would doubtless provide a convenient method for the differentiation in the activities of the various parts of a catalyst surface.

The structural nature of adsorption compounds has likewise been demonstrated by Langmuir (*loc. cit.*) in his studies on the "clean up" of electric lamps. Carbon monoxide was found to be strongly adsorbed at low temperature by tungsten and attempts to desorb the gas resulted in the fracture of the bonds holding the superficial tungsten atoms to the metal and the volatilisation of the whole group WCO. At bigher temperatures however the W—CO union becomes weaker and the gas may be desorbed unchanged. Again he noted that small quantities of oxygen inhibit by selective adsorption the dissociation of hydrogen at the surface of a hot tungsten wire but the adsorbed oxygen is not as readily reduced as the oxide WO_3. In the case of oxygen adsorbed on charcoal the —C—O union appears to undergo a series of interesting changes. At very low temperatures according to Dewar a small fraction of oxygen may be adsorbed and desorbed from a charcoal surface, the union being apparently between the oxygen molecule and the charcoal and relatively feeble.

At 0° to 100° C. part of the oxygen adsorbed on charcoal is endowed with catalytic properties, thus it will readily oxidise oxalic acid, amino acids, cystein and other similar compounds, whilst we would anticipate similar reactions if the oxygen molecule were now adsorbed in such a way as to cause a breakage of one of the two bonds O=O → O—O. At high temperatures, as is well known,

oxygen is irreversibly adsorbed by charcoal and is only desorbed in the form of the gaseous oxides of carbon. The oxygen-carbon union now exceeds in strength the union between the superficial carbon and the underlying atoms.

Two further lines of attack on the problem of orientation of the adsorbed layer at a gas-solid interface may be briefly mentioned.

We have noted that the evidence for orientation at a gas-liquid interface is very convincing. Iredale (*Phil. Mag.* XLV. 1088, 1923) has shown that the areas occupied by molecules on the surface of liquid mercury are sensibly the same as those occupied by the molecules on a water surface, thus the orientation of molecules condensing from a vapour on the surface of liquid mercury is identical with the orientation on water. There is no reason to suspect that if the liquid mercury surface were replaced by a solid metal surface the orientation of the adsorbed molecules would in any way be affected. Again the X-ray examination of the layers of fatty acids solidified on mica (Müller and Shearer, *J.C.S.* CXXIII. 156, 1923) has revealed the fact that the fatty acid molecules adsorbed on the mica are stratified in regular orientated molecules, the direction of orientation being perpendicular to the plane of the mica.

Evidence of attachment of an organic molecule to a metal surface by a particular group in the molecule is not only provided from surface tension data on the surface of liquid mercury but is also to be noted in the phenomenon of displacement of one liquid by another from a surface. The hydrocarbons adhere to metals much less tenaciously than molecules containing polar groups such as —COOH and —OH. Thus we find that a hydrocarbon may be removed from a metal surface by displacement with alcohol and also that the lubricating properties of a hydrocarbon are materially affected by the addition of hydrocarbon compounds containing polar groups (Hardy, *Proc. Roy. Soc.* A, C. 550, 1922, A, CI. 487, 1923).

Again Constable and Palmer have investigated the rate of decomposition of a number of primary alcohols into aldehydes and hydrogen at the surface of copper. In this case it is only the terminal —CH_2OH group which undergoes decomposition. It was found that the temperature coefficient for the rates of decomposition of all the alcohols was identical (1·540), supporting the hypothesis

that this group was the only one taking part in the processes occurring at the surface of the copper.

10. The properties of gases in the adsorbed layer.

We have noted that adsorption is the result of attainment of equilibrium between the processes of condensation and evaporation and consequently we may ascribe to the adsorbed molecule a certain mean length of life on the surface of the adsorbing agent. The adsorbed molecule may be regarded as oscillating on the surface of the adsorbing agent, the kinetic energy being provided both by collisions of gas molecules as well as by impulses imparted by the underlying adsorbing molecules. If we assume that the distribution of energy in the adsorbed gas layer obeys the Boltzmann-Maxwell distribution law obtaining for homogeneous gases then the fraction of the total number of molecules which at any time possess sufficient energy to escape from the surface is

$$e^{-\frac{Q}{RT}},$$

where Q is equal to the latent heat of adsorption at that particular temperature. If the mean length of life of such a molecule which can escape or "active" molecule on the surface be t or $\frac{1}{r}$, then the rate of evaporation will be given by

$$\frac{dx}{dt} = re^{-\frac{Q}{RT}}.$$

It is possible that t the mean length of life of the active molecule as well as the total number of such available for evaporation $e^{-\frac{Q}{RT}}$ is a function of the temperature. Thus the length of life of an active molecule on the surface is not directly obtainable from the vapour pressure temperature curve for a unimolecular film, but investigations on this point would prove of great interest.

If we assume an equal probability for all adsorbed molecules to evaporate we can readily calculate the average life of a molecule on the surface between the acts of condensation and re-evaporation from the rate of condensation and the amount of surface covered. Such calculations have been made by Langmuir (*J.A.C.S.* XL. 1393, 1918) who gives the following data for the mean length of life in

seconds required for the evaporation of 1 gm. molecule of the gas from 1 sq. cm. of surface:

Gas	Surface Liquefied gas		Surface Mica		Surface Glass
	$T=90°$ K.	$T=155°$ K.	$T=90°$ K.	$T=155°$ K.	$T=90°$ K.
N_2 ...	0·30	0·013	440,000	2×10^6	330,000
CH_4...	5·50	0·070	24,000	140,000	10,000
CO ...	0·50	0·021	1,500,000	480,000	190,000
Ar ...	0·96	0·022	92,000	—	73,000
O_2 ...	1·24	0·029	80,000	—	78,000
CO_2...	—	16·500	—	9,000	—

It will be noted that the adhesional forces between nitrogen and methane increase more rapidly with the temperature on mica than the increase in the kinetic energy of the molecules, resulting in a relatively longer life at high temperatures.

For the average length of life of carbon monoxide on platinum he obtained the following data:

Temp. ° K.	Average life in seconds	Temp. ° K.	Average life in seconds
300	$1{\cdot}2\times10^{11}$	650	·038
350	$5{\cdot}8\times10^{7}$	700	·0066
400	$1{\cdot}9\times10^{5}$	750	·0014
450	2200	800	·00038
500	63	900	·00004
550	3·30	1000	·00001
600	·30		

If the surface be only partially covered (a fraction θ) with adsorbed molecules the rate of evaporation will evidently be equal to $\nu\theta^n$, where n is the valency of the adsorbed molecule and ν the specific rate of evaporation per sq. cm. of surface covered. The rate of condensation is equal to

$$\alpha p\,(1-\theta)^n,$$

where p is the partial pressure of the gas, hence

$$\frac{1}{\nu}=t=\frac{\theta^n}{\alpha p\,(1-\theta)^n}.$$

Thus from a knowledge of the amount adsorbed at various temperatures at constant pressure the alteration in length of life of the adsorbed molecules may be computed.

The most curious property of gases in the adsorbed film is that of great or enhanced chemical activity. In most cases only a fraction of the molecules striking a catalyst surface undergo decomposition or chemical reaction, the majority of the molecules re-evaporate unchanged. Of those cases in which every molecule of a reactant striking a surface undergoes decomposition or chemical change may be mentioned the decomposition of ozone (Strutt, *Proc. Roy. Soc.* A, LXXXVII. 302, 1912) at silver surfaces, the decay of active nitrogen at copper surfaces and the combination of hydrogen atoms at platinum surfaces. The adsorption of a molecule is as we have noted accompanied by a heat evolution and an adsorption compound is formed between the gas and adsorbate. The adsorbed gas in the adsorption compound must be regarded as distorted and in this distorted form is more reactive. In considering homogeneous chemical reactions we must, as indicated by Arrhenius, postulate the existence of passive and active or excited molecules. The active or excited molecules are those which react on collision and probably consist of distorted molecules or molecules in a higher quantum state than the normal. The excess internal energy of the active or excited molecules which is the energy of excitation or critical energy increment may be determined with the aid of the Arrhenius equation from the temperature coefficient

$$\log \frac{k_1}{k_2} = \frac{E}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right),$$

and is supplied in gaseous reactions by collision with other fast moving molecules. Thus all collisions in a gas are not perfectly elastic, but in some, part of the energy of translation is converted on impact into the quantised internal energy of activation or excitation (E), the fraction of such active or excited molecules present being given by the Boltzmann-Maxwell equation

$$N_a = Ne^{-\frac{E}{RT}}.$$

In the case of the adsorbed molecules a certain number of these as we have seen are capable of re-evaporating. If E_v be the energy

required for evaporation the fraction capable of evaporation at any time will be $e^{-\frac{E_v}{RT}}$.

For reaction, e.g. the dissociation, of hydrogen at the surface of nickel, the fraction of molecules capable of so dissociating will be

$$e^{-\frac{E_{diss.}}{RT}},$$

where $E_{diss.}$ is the energy of excitation required for the dissociation of the adsorbed hydrogen.

Evidently the catalytic efficiency will depend upon the relative values of $E_{diss.}$ and E_v. Small values of the former and large values of the latter would indicate a high catalytic efficiency. The critical energy increment for a catalytic surface reaction cannot be determined directly from the temperature coefficient since as we have noted at any definite pressure the surface concentration will in general become less as the temperature is raised so that the apparent increase in velocity is in reality smaller than the true increase in velocity for the surface reaction when calculated per sq. cm. of covered surface. In addition as we have noted the rate of a surface reaction involves two terms, the number of active or excited molecules and the length of life of such an excited molecule. We are not necessarily justified in the assumption that the life of the excited molecule is independent of the temperature. Nevertheless the temperature coefficients of many reactions give us some idea of the energies of activation required, these are in all cases less that required for the simple gas reaction. This phenomenon is only explicable on the assumption that molecules can be excited in various stages. Thus in the reaction

$$H_2 \rightarrow 2H—Q$$

the hydrogen molecule must be excited to a definite level to promote disruption, the quantity of energy to be supplied is some 96,400 calories per gm. molecule.

On a catalyst X however we obtain the following series of reactions:

(1) Adsorption on impact of a hydrogen molecule on two spaces on the elementary lattice.

(2) Excitation of the adsorption compound H_2X_2 to two

possible levels (*a*) producing re-evaporation of the adsorbed molecule, (*b*) producing dissociation of the adsorption compound H_2X_2 into HXHX.

(3) The liberation of atomic hydrogen by further excitation of the adsorption compound HX may be produced but the amount of energy required for this purpose is very large and normally such reactions do not occur below 1000 ° K.

Thus we note that owing to the large affinity of hydrogen atoms for each other in the gaseous equilibrium

$$H_2 \rightleftarrows 2H,$$

at all reasonable temperatures the molecular state almost completely preponderates, yet on surfaces the equilibrium expressed by the compounds

$$X_2H_2 \leftrightarrows 2HX \qquad (1)$$

may result in the relatively high concentration of HX or adsorbed atomic hydrogen, which although not so reactive as gaseous atomic hydrogen yet represents in activity a stable intermediate form between molecular hydrogen and tbe atomic gaseous form. The catalytic efficiency of a metal for hydrogenations thus rests as far as the hydrogen is concerned on firstly the equilibrium of the surface compounds according to (1), secondly the rate at which such equilibrium is attained and thirdly the reducing power of the adsorbed atomic hydrogen as measured by the decrease in free energy occurring during the process of adsorption or conversely the energy of excitation required to form HX from X_2H_2.

11. Influence of Catalyst on Molecular Excitation.

An "active" molecule or a complex of molecules is now generally regarded as one which has been raised either by the adsorption of radiation by an α particle, electron or molecular collision to a higher quantum state.

The active molecule must be regarded as in a state of strain or as a distorted molecule and the ease of distortion or the energy of activation will be dependent on the molecular structure. The following values for the energies of activation as calculated from the temperature coefficients indicate clearly the effect of substitution in a simple molecule on the energy of activation.

Reaction (Nicoll and Cain, *J.C.S.* LXXXIII. 470)

$$RC_6H_4N_2Cl + H_2O \rightarrow RC_6H_4OH + N_2 + HCl.$$

R	*E* cals. per gm. mol.
H	24,300
o. CH_3 ...	25,100
m. CH_3 ...	22,900
p. CH_3 ...	27,900
p. SO_3H ...	28,200
m. NO_2 ...	30,500

Reaction

EtOOC. COCHR. COOEt → CO + EtOOCCHR. COOEt.

R	*E* cals. per gm. mol.
$—OC_2H_5$ ...	35,800
$—CH_3$	33,300
$—CH_2COOC_2H_5$	35,400
$—C_6H_5$	44,300

Instead of introducing substituent groups into a molecule we may dissolve a reactant in a solvent and the energy of activation of decomposition of the complex reactant-solvent will vary in a similar manner as we alter the solvent as exemplified by the data of von Halban (*Zeit. Phys. Chem.* LXXVII. 129, 1909) on the decomposition of triethylsulphine bromide, the energies of activation being calculated without correction for the possible alterations with the temperature of the concentration of the complex undergoing reaction.

Solvent	*E* cals. per gm. mol.
Nitrobenzene ...	28,530
Tetrachlorethene	30,390
Amyl alcohol ...	33,190
Propyl alcohol ...	33,750
Benzyl alcohol ...	35,920

and by Cox (*J.C.S.* CXIX. 142, 1921) on the addition of aniline to bromacetophenone.

Solvent	*E* cals. per gm. mol.
Benzene ...	8,088
Chloroform ...	10,760
Nitrobenzene ...	13,470
Ethyl alcohol ...	13,910
Benzyl alcohol	14,290

We should thus anticipate that the energy of activation of the adsorption compounds in heterogeneous catalysis would vary with the nature of the catalyst. It is however, as we have seen, a difficult matter to determine the value of *E* from the temperature coefficient alone, for the surface of the catalyst may not be equally covered with the reactant over the temperature range of investigation and in addition, as we have had occasion to note, the surface of the catalyst is by no meaus homogeneous.

Nevertheless attempts may be made in a few cases to show how *E* the energy of activation varies with the nature of the adsorption compound. Stewart and Edland (*J.A.C.S.* XLV. 1014, 1923) have shown that ethylene and bromine when dry react at 0° C. only on the walls of the reaction vessels. In the laboratory at Cambridge Norrish (*J.C.S.* CXXIII. 3006, 1923) found that the velocity of catalysis at 0° of this reaction varied with the nature of the surface of the reaction vessels. The following values for the velocity constants calculated as a bimolecular reaction were obtained.

Surface	*k* 0° C.
Paraffin wax ...	·0030
Cetyl alcohol ...	·0266
Glass	·0506
Stearic acid ...	·0864

Assuming that all the surfaces are equally uniform and equally covered under the pressures (11·5 mm.) and at the temperature 0° C. at which the reaction is carried out it is evident that the

number of molecules excited and reacting per second is greatest on the highly polar stearic acid surface, or the energy of activation of the surface compound on this material must be the smallest. More recently Norrish has shown that ethylene and chlorine behave in a similar manner, that wet glass is more catalytically active than dry glass and that the activity of the paraffin wax may be augmented by the addition of an adsorbable alcohol such as propyl alcohol to the reaction mixture.

On the assumption that the catalytically active area covered by the reactant remains unchanged over the experimental temperature range Hinshelwood and Topley (*J.C.S.* CXXIII. 1014, 1923) have determined the following energies of activation from the temperature coefficient and the relative reaction velocities for the decomposition of formic acid according to the equation

$$HCOOH \rightarrow CO_2 + H_2$$

at various surfaces. Their data are summarised as follows:

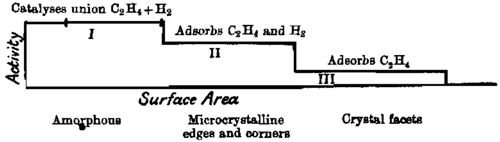
Surface	*E* cals. per gm. mol.	*k* at 200° C.
Duroglass ...	24,500	$2{\cdot}5 \times 10^{-7}$
Gold	23,500	$9{\cdot}2 \times 10^{-6}$
Silver	31,000	$1{\cdot}0 \times 10^{-5}$
Platinum ...	22,000	$4{\cdot}4 \times 10^{-4}$
Rhodium ...	25,000	$2{\cdot}4 \times 10^{-3}$
Palladium freshly treated with an oxidising agent	39,000	$1{\cdot}0 \times 10^{-3}$
Palladium containing occluded H_2	33,000	—

It is evident in this case that the velocity of reaction is not dependent on the energy of activation alone. This as we have seen is due to the fact that catalysis is not proceeding over the whole area of the catalyst but only at highly localised patches which in the case of palladium are evidently much more extensive than on duroglass. The energy of activation is calculated from the influence of temperature on the reaction velocity proceeding at an unknown area of surface; whilst in the case of the combination of ethylene and the halogens it was tacitly assumed that a surface covered with molten fatty acids or alcohols would in all cases exhibit a

similar uniformity and thus not only a constant area of surface but also a constant area of catalytically active surface.

12. The effect of poisons on catalytic activity.

Maxted (*J.C.S.* CXXI. 1760, 1922), who has examined the effect of progressive additions of poisons to catalysts such as platinum, came to the conclusion that the retardation in catalytic activity was proportional to the amount of poison adsorbed. A critical examination of his own data indicate however that this linear poisoning law is by no means correct. The addition of small quantities of poison may cut down or stop completely the catalytic activity whilst on increasing the concentration of poison further adsorption on the less active areas may readily be detected. On the hypothesis of patches of varying activity on the catalyst surface the poison will first be adsorbed on the more reactive spaces which are catalytically active as well. Confirmation of this hypothesis is to be obtained from the work of Adams on the promotion of platinum in the reduction of organic substances (*J.A.C.S.* XLV. 1073, 1923, XLVI. 1675, 1924) where an increase in velocity was observed on the addition of small amounts of certain salts followed by poisoning on further increase in the salt concentration. Pease has examined the effect of carbon monoxide and mercury vapour on a copper catalyst promoting the hydrogenation of ethylene. It was found that a small quantity of these poisons destroyed the catalytic activity entirely but only reduced slightly the adsorption of the two reacting gases. Evidently the very active areas adsorb both gases and effect catalysis; less active areas adsorb both gases but do not promote catalysis and still less active areas adsorb ethylene but not hydrogen. Diagrammatically we may represent our catalyst surface as consisting of three types of surface.



From data obtained at Cambridge and at Princeton the relative areas of the three forms of catalyst surface present in a carefully prepared copper catalyst are (1) *ca.* 0·01 °/₀, (2) 40 °/₀, (3) 60 °/₀.

Bodenstein and Ohlmer's (*Zeit. Phys. Chem.* LIII. 160, 1905) investigation on the catalytic oxidation of carbon monoxide at the surface of crystalline and fused quartz likewise indicate that the differentiation in surface of activity due to atomic arrangement may lead to a difference in the reaction mechanism. On the more active fused quartz we find that carhon monoxide is strongly adsorbed (probably however on patches of limited area) and the reaction rate is accordingly given by

$$\frac{dx}{dt} = \kappa \frac{O_2}{CO}.$$

On the crystalline quartz on the other hand the gases are but feehly adsorbed and the rate is governed by the probability of reaction between oxygen atoms and carbon monoxide on adjoining elementary spaces or

$$\frac{dx}{dt} = \kappa \sqrt{(O_2)}\,(CO).$$

The differentiation in surface activity of a particular surface due to the atomic configuration allows us to effect certain selective catalytic operations the possibilities of which have been demonstrated by Vavon and Husson (*C.R.* CLXXV. 277, 1922) (p. 143).

Acetophenone does not undergo hydrogenation with such ease as cyclohexene. In the presence of active platinum black both these substances may be hydrogenated, but if the very active areas of platinum black be poisoned by the addition of carbon disulphide acetophenone is no longer hydrogenated but cyclohexene will be. The hydrogenation of cyclohexene can naturally be prevented by the further addition of carbon disulphide to the catalyst which is now inert except in respect to the hydrogenation of nitrobenzene which undergoes reduction with great facility. This reaction can be stopped by an excessive dose of the poison.

The selective poisoning of the very active areas may be beneficial in certain cases. Thus Armstrong and Hilditch (*Proc. Roy. Soc.* A, XCVII. 262, 1920) noted that small quantities of water vapour in the dehydrogenation of alcohol on a copper surface

$$(1)\quad C_2H_5OH \rightleftarrows CH_3CHO + H_2,$$

greatly reduced the secondary decomposition of the aldehyde

$$(2)\quad CH_3CHO \rightleftarrows CH_4 + CO.$$

An investigation of the temperature coefficients of both these reactions would probably reveal the fact that $E_2 > E_1$ (for $E_1 \frac{\kappa_{\theta+10}}{\kappa_\theta} = 1{\cdot}54$ approximately; E_2 has not been evaluated) and that only very active patches would permit of the attainment of this value.

CHAPTER VI

THE LIQUID-SOLID INTERFACE

1. Adsorption at solid surfaces.

We have already had occasion to note that on exposure of a fresh solid surface to a gas adsorption takes place and the surface becomes covered with a film of the gas.

On the immersion of a solid surface in a liquid the solid will be already coated with a gas film prior to immersion (unless a surface is freshly formed by condensation or by cleavage in the liquid), which must be removed before actual wetting of the solid takes place. Solids which adsorb liquids preferentially to gases are wetted after a period of immersion short or prolonged, whilst those in which the gas-solid adhesional forces are greater than those of the liquid-solid are not so wetted.

Thus glass which adsorbs the various constituents of the air more readily than it adsorbs mercury is not wetted by the metal, but if the adsorbed gas be removed from the surface, e.g. with the aid of a high vacuum such as obtains in a MacLeod gauge, the mercury may be caused to adhere to the glass.

2. Surface energy of solid-liquid interfaces.

As in the case of the solid-gas interface it is a very difficult matter to determine the value of the surface energy of the solid-liquid interface, viz. σ_{sl}.

Attempts have been made to compute this value by the measurement of the solubility of small particles of the solid (see p. 37) notably by Ostwald (*Zeit. Phys. Chem.* XXXIV. 495, 1900), Freundlich (*Kapillarchemie*, 1920, p. 143), Hulett (*Zeit. Phys. Chem.* CCCLXXI. 385, 1901), Hulett and Allen (*J.A.C.S.* XXIV. 667, 1902), W. J. Jones (*Ann. der Phys.* IV. 441, 1913) and Jones and Partington (*J.C.S.* CVII. 1079, 1915), Dundon (*J.A.C.S.* XLV. 2479, 2658, 1925) and others.

On analogy with the surface tension effects in liquids we may consider that there will be an excess pressure inside a small solid sphere immersed in a liquid equal to

$$\frac{2\sigma_{sl}}{\rho r},$$

where σ_{sl} is the interfacial surface energy, ρ the density of the solid and r the sphere radius.

The work done in transferring an amount of the material δw from a sphere of radius r_1 to one of radius r_2 will accordingly be

$$\frac{2\sigma_{sl}}{\rho}\left\{\frac{1}{r_1}-\frac{1}{r_2}\right\}\delta w.$$

If the osmotic pressures of the solutions with which the two spheres are in equilibrium be Π_1 and Π_2 respectively the transfer of δw of the solute from one solution to another will necessitate the expenditure of energy equal to

$$\delta w\, RT \log\frac{\Pi_1}{\Pi_2} = \delta w\, RT \log\frac{c_1}{c_2}$$

for dilute solutions, i.e. for relatively insoluble salts.

Since the two systems are in equilibrium

$$\delta w\, RT \log\frac{c_1}{c_2} = \frac{2\sigma_{sl}}{\rho}\left\{\frac{1}{r_1}-\frac{1}{r_2}\right\}\delta w \quad \text{or} \quad RT\log\frac{c_1}{c_\infty} = \frac{2\sigma_{sl}}{\rho r},$$

where c_∞ is the solubility of large crystals ($r=\infty$) of the salt. Hulett found for grains of calcium sulphate, where $r = \cdot00003$ cm. a solubility as determined by conductivity measurements $c_1 = 18{\cdot}2$ millimols per litre. The normal solubility c_∞ obtaining for grains where $r > 0{\cdot}0002$ cm. is 15·33 millimols per litre. From these data $\sigma_{sl} = 1100$ ergs per sq. cm.; in the case of barium sulphate σ_{sl} was found to be 1300.

The more recent experiments of Dundon have indicated that Hulett's value for calcium sulphate is much too high, doubtless owing to the effect of grinding on the water content of the decahydrate. Dundon obtained the following values for a series of salts.

Substance	$\sigma_{S.\,water}$
PbI_2 ...	130
$CaSO_4 2H_2O$	370
Ag_2CrO_4 ...	575
PbF_2 ...	900
$SrSO_4$ ...	1400
$BaSO_4$ ...	{1250 / 3000
CaF_2 ...	2500

There exists a rough proportionality between the surface tension and the hardness as well as an inverse proportionality to the molecular volume of the solid.

The validity of the premises on which such calculations are founded can not only be called to question by the considerations that have already been discussed concerning the solid-gas interface, but a further complication is introduced when the substance whose solubility is being determined is an electrolyte. The surfaces of the crystal adsorb not only the water in which they are suspended but also the ions of the salt in solution (see p. 185). At equilibrium there is a dynamic interchange between the ions in solution and those on the surface. In the vaporisation of an ionised salt, such as sodium chloride, the positive and negative ions evaporate as doublets except at very high temperatures when the kinetic energy of the individual ions is sufficient to rupture the electrostatic hond between the doublet. In solution however it is probable that the removal of the surface ions by reaction with the water or by solution and the re-deposition of the ions by diffusion does not necessarily occur in doublets; thus radium ions may replace barium ions at the surface of a crystal of barium sulphate immersed in a solution of a radium salt and such replacement may take place, not through the removal of a molecule of barium sulphate and substitution of the same, but by the removal of a barium ion from the space lattice and its replacement by a radium ion. In a similar manner crystals of silver chloride will adsorb silver ions into the space lattice of the crystal—presumably where the chlorine ions are exposed. Under these circumstances the crystal will acquire an electric charge continually varying in sign fluctuating as a positive or negative ion is in excess on the surface. The effect of this fluctuation in charge may be calculated if it be assumed that the electric charge is spread uniformly over the surface. It will then produce an expanding pressure equal to

$$\frac{\epsilon^2}{8\pi\kappa r^4},$$

where ϵ is the electric charge, κ the S.I.C. of the medium and r the radius of the crystal (Lewis, *Koll. Zeit.* v. 91, 1909; Knapp, *Trans. Faraday Soc.* May, 1921).

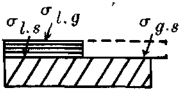
The effect of curvature or surface energy on the osmotic pressure and thus on the solubility is thus removed when

$$\frac{2\sigma_{sl}}{\rho r} = \frac{\epsilon^2}{8\pi\kappa r^4} \quad \text{or} \quad r = 3\sqrt{\frac{\epsilon^2 \rho}{16\pi\kappa\sigma_{sl}}}.$$

In many cases an electrical double layer is formed (see p. 210) which enhances the difficulty of calculation.

3. The displacement of liquids at solid surfaces.

The conditions under which a liquid will wet or displace a gas in contact with a solid surface can most readily be determined by consideration of the changes in surface energy due to an increase in the area of contact between liquid and solid. If the surface energies between liquid-gas, liquid-solid, gas-solid be denoted by σ_{lg}, σ_{ls} and σ_{gs} respectively, and a unit area of extension of the liquid over the surface of the solid is imagined to take place, we increase the surface energy liquid-solid by σ_{ls}, simultaneously increase the surface energy liquid-gas by σ_{lg} and decrease the surface energy gas-solid by σ_{gs}. The decrease in the free surface energy is accordingly



$$\sigma_{gs} - \{\sigma_{ls} + \sigma_{lg}\}.$$

If there is a decrease in the free surface energy the liquid will continue to displace the gas from the surface of the solid, i.e. the solid will be wetted by the liquid if

$$\text{(i)} \quad \sigma_{gs} > \sigma_{ls} + \sigma_{lg}^{*}.$$

Similarly a second liquid (2) will displace another liquid from the surface if

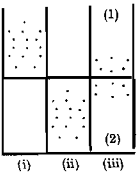
$$\text{(ii)} \quad \sigma_{1s} > \{\sigma_{2s} + \sigma_{21}\}.$$

It is clear from a consideration of equation (i) that liquids of low surface tension, i.e. small values of σ_{lg} are more likely to wet solids than liquids of high surface tension. Thus the organic hydrocarbons of low surface tension readily wet most solid surfaces; water will wet but a limited variety of surfaces whilst the displacement of the adsorbed air film from solids by mercury is a comparatively rare occurrence. We find also (equation (ii)) that oil will displace

* This displacement only takes place by a process of evaporation and condensation not by spreading, see p. 91.

water from the surface of metallic sulphides but that the converse takes place at the surface of powdered quartz, a phenomenon which is the basis of the ore flotation process.

Under the conditions just discussed the solid surface is rigid whilst the two liquids are brought into contact with the solid. The effect of preferential wetting of a solid surface by liquids can also be investigated by the examination of the distribution of fine solid particles placed near the interface of two immiscible liquids.



If $\sigma_{s2} > \sigma_{s1} + \sigma_{12}$ the solid particles will be preferentially wetted by the first liquid and both the second liquid and the interface will be clear and free from solid (i).

If $\sigma_{s1} > \sigma_{s2} + \sigma_{12}$ the second liquid will contain all the solid particles (ii), and finally if

$\sigma_{12} > \sigma_{s1} + \sigma_{s2}$ or if no one surface energy is greater than the sum of the two others, the particles will collect at the interface between the two liquids, the solid in this latter case increases the miscibility of the two liquids, since both liquids are adsorbed by the solid and exist in the adsorption layer as a homogeneous mixture (iii). (See p. 105, Ch. IV.)

Experiments illustrating these various possible reactions have been carried out notably by Reinders (*Zeit. Koll. Chem.* XIII. 235, 1913) and by Hofmann (*Zeit. Phys. Chem.* LXXXIII. 385, 1913). Finely divided calcium sulphate is preferentially wetted by water in the presence of liquids, such as chloroform and benzene which are frequently termed non-polar or slightly polar. Silver iodide suspensions in water will go into the dineric interface in contact with ether, chloroform and benzene, but are removed from the water by preferential wetting in the case of butyl and amyl alcohols, whilst the reverse holds true in the case of aqueous suspensions of arsenious sulphide.

The state of aggregation of the solid occasionally affects the interfacial surface tensions sufficiently to alter the distribution between two immiscible liquids. In the case of gold, blue gold will pass to the dineric surface ether-water, whilst brown gold will remain in the aqueous phase. A protective colloid (see p. 200)

which affects the interfacial surface tension will also affect the distribution, since the solid-liquid interface of the original solid has been replaced by that of the protective agent liquid interface. Most protective agents for aqueous suspensions are hydrated substances and as a result the material thus protected usually passes into the aqueous phase.

4. The heat of adsorption.

It has already been noted that in the case of the easily liquefiable gases adsorption in multimolecular layers occurs, the heat of adsorption of such a vapour at the point of saturation is evidently identical with the heat of wetting. Calorimetric determinations of the heat evolved on wetting dry solid powders with various liquids have been made, notably by Gaudechon (*C.R.* CLVII. 207, 1913), Pouillet (*Ann. Chim. Phys.* XX. 141, 1822), Junck (*Pogg. Ann.* CXXV. 292, 1865), Chappuis (*Wied. Ann.* XIX. 21, 1883), Fitzgerald (*Nature*, XLIX. 293, 316, 1894), Lagergren (*Kgl. Vetenskaps Akad.* XXIV. B, 1898). There is a wide variation in the magnitude of the heats of adsorption of a liquid, both with the nature of the adsorbing material and adsorbed liquid, as can be noted both from the data on the adsorption of vapours (see p. 149) and the following data of Gaudechon.

Liquid	Heat of adsorption in cals. per gm.		
	Adsorbing material		
	Alumina	Quartz	Sugar charcoal
H_2O	12·6	15·3	3·9
CH_3OH ...	11·0	15·3	11·5
$HCOOH$ ...	12·0	14·5	*ca.* 12·0
CH_3COOH ...	9·3	13·5	6·0
C_3H_7COOH	7·8	13·5	6·0
CCl_3H ...	9·0	8·0	2·3
C_6H_6 ...	5·8	8·1	4·2
CS_2	1·7	8·6	4·0
CCl_4 ...	1·8	8·1	1·5
C_6H_{14} ...	1·2	3·1	0·4

A more accurate investigation of the heats of wetting of known areas of solids by various liquids over an extended temperature range is highly desirable since it offers a promising method of

testing the validity of the Nernst heat theorem in connection with the thermodynamics of the surface phase. As we have already had occasion to observe the surface tension or free surface energy is related to the total surface energy, which can be determined calorimetrically, by means of the Gibbs-Helmholtz equation $\sigma - u = T\frac{d\sigma}{dT}$. According to the Nernst heat theorem $\underset{T=0}{\mathrm{Lt}}\frac{du}{dT} = 0$ and $\underset{T=0}{\mathrm{Lt}}\frac{d\sigma}{dT} = 0$. The thermal changes should on analogy with Debye's investigations on the energy content of substances at low temperatures be expressible in the form $u = u_0 - aT^4$, where a is determinable from the heat capacity of the surface film, and the temperature coefficient of the heat of wetting should decrease rapidly as we approach the absolute zero. Furthermore it is evident that at this temperature the free and total surface energies should be identical in value, the total surface energy sinking first slowly and then rapidly as the critical temperature is reached. Confirmation likewise of the assumption $\underset{T=0}{\mathrm{Lt}}\frac{d\sigma}{dT} = 0$ or that the temperature coefficient of the free surface energy should fall as we approach the absolute zero is lacking, but the relationship does not appear to hold for the gases nitrogen, argon and hydrogen over the temperature range already investigated. In addition the relationship between the free and total surface energies which should obtain at low temperatures, viz. $\sigma = u_0 + \frac{aT^4}{3}$ is markedly different to that obtained at high temperatures (see p. 19).

Very few attempts have been made to estimate the heat of adsorption per sq. cm. of adsorbing surface owing to the difficulty in computing the area of a porous adsorbent such as charcoal.

Parks (*Phil. Mag.* VI. 4, 247, 1902) has estimated the heat of adsorption of water on silica at 7° C. as 0·001005° calorie per sq. cm. Gaudechon's quartz would thus expose a surface of 1450 sq. metres per gm., whilst Koehler and Matthews (*J.A.C.S.* XLVI. 1166, 1924) obtained a value of somewhat less than $1{\cdot}69 \times 10^{-6}$ cals. per sq. cm. for dry lead sulphate.

A wide variation in the hypothetical surface of charcoals is cited in the literature. Williams (*Proc. Roy. Soc. Edinburgh*, XXXIX.

48, 1918) computes for charcoal evacuated at a relatively low pressure a value of 131 sq. metres per gm., Lowry and Hulett (*J.A.C.S.* XLII. 1393, 1920) 200 sq. metres, Lamb (*J. Ind. and Eng. Chem.* XI. 420, 1919) 1000 sq. metres, and Harkins and Ewing (*J.A.C.S.* XLIII. 1798, 1921) less than 120 sq. metres.

The most exhaustive examination of the surface areas of various forms of charcoal has been made by Paneth and Radu (*Ber.* LVII. 1221, 1924) who, on the assumption that a saturation maximum is obtained when the surface of charcoal is covered with a unimolecular layer of adsorbate, obtained the following values.

Adsorbate	Animal charcoal		Wood charcoal	
	Mols. adsorbed per gm. $\times 10^{-20}$	Surface in sq. metres	Mols. adsorbed per gm. $\times 10^{-20}$	Surface in sq. metres
Methylene blue...	3·94	220	1·81	101·0
Methyl green ...	2·56	190	1·26	95·0
Ponceau 2*R* ...	1·90	119	0·98	56·2
$Pb(NO_3)_2$ ...	6·07	123	2·16	46·2
Acetone	18·50	452	11·00	268·0

Adsorbate	Bone charcoal		Sugar charcoal activated	
	Mols. adsorbed per gm. $\times 10^{-20}$	Surface in sq. metres	Mols. adsorbed per gm. $\times 10^{-20}$	Surface in sq. metres
Methylene blue...	1·14	68·0	0·44	24·8
Methyl green ...	1·54	114·0	0·26	19·2
Ponceau 2*R* ...	1·65	103·0	—	—
$Pb(NO_3)_2$ ...	4·50	97·8	0·61	13·2
Acetone	14·70	359·0	2·29	55·9

The high values obtained with acetone were attributed to penetration within the pores of the charcoal.

An interesting series of values for the specific surfaces of various artificial silks was likewise obtained with the aid of methylene blue. The following data indicate the wide variations in specific surface.

Type of silk	Nitro-silk	Cupro-cellulose	Acetic silk
Specific surface	1820	456	28

5. Surface compression in adsorption.

The determination of the density of charcoals by immersion in liquids has revealed a singular fluctuation of the apparent density with the nature of the liquid employed. The data obtained by *Cude and Hulett (J.A.C.S.* XLII. *391, 1920), Harkins and Ewing* (*ibid.* XLIII. 1794, 1921), and Williams (*Proc. Roy. Soc.* A, XCVIII. 224, 1920), are summarised in the following table, together with the compressibilities of the liquids for comparison.

Apparent specific volumes				
Immersion liquid	Williams. Fine charcoal	Cude and Hulett. Coarse charcoal	Harkins. Gas-mask charcoal	Compressibility $\beta \times 10^6$ at 20° C.
Water	0·511	0·539	0·466	46
Carbon disulphide	—	0·504	0·420	90
Benzene	—	0·556	0·432	92
Chloroform ...	0·461	—	0·434	128
Ether	—	—	0·408	183

The hypothesis that liquids in contact with charcoal were actually compressed on the surface of the solid was originally suggested by Lagergren (*Bihang till k. Svenska Vet. Akad. Handl.* 24, II. 4, 1898) who assumed the existence of surface pressures of the order of 10,000 atmospheres. Lamb and Coolidge (*J.A.C.S.* XLII. 1146, 1920) considered that the net heat of adsorption was due to compression alone and that with charcoal the compressive force was substantially the same for all liquids, viz. 37,000 atmospheres. A similar conclusion was arrived at by Harkins and Ewing.

Williams (*loc. cit.*) who has investigated this hypothesis in detail ascribes the surface compression at the charcoal liquid interface both to the liquid and to the solid. The internal pressure of a liquid may be represented by the $\frac{a}{v^2}$ term of the Van der Waals equation. Attributing a similar cohesive internal pressure to the charcoal $\frac{a_1}{v_1^2}$, we can assume that the attraction of the liquid for

the solid may be represented by a term $\sqrt{\frac{a}{v^2}} \times \sqrt{\frac{a_1}{v_1^2}}$. Such an assumption however is only justified on the assumption that no species of chemical action takes place between liquid and solid.

If the true specific volume of the solid be v and has adsorbed on it α gms. of the liquid of specific volume, in the compressed state, of v_2 the total volume of solid and film will be

$$v + \alpha v_2.$$

If v_0 be the observed volume of the solid calculated without regard to α, and v_1 the specific volume of the uncompressed liquid the total volume will be

$$v_0 + \alpha v_1.$$

Hence $$v + \alpha v_2 = v_0 + \alpha v_1,$$

or $$v = v_0 + \alpha (v_1 - v_2).$$

In his experiments Williams obtained the following values:

$$v_0\, H_2O = 0{\cdot}511, \quad v_0\, CCl_3H = 0{\cdot}461,$$

$$\alpha\, H_2O = 0{\cdot}75 \text{ c.c.}, \quad \alpha\, CCl_3H = 0{\cdot}85 \text{ c.c.},$$

whence we obtain with the aid of the above equation

$$0{\cdot}85 \frac{v_{2\,CCl_3H}}{v_{1\,CCl_3H}} - 0{\cdot}75 \frac{v_{2\,H_2O}}{v_{1\,H_2O}} = 0{\cdot}05.$$

From a knowledge of the corresponding internal pressures and compressibilities of the two liquids Williams finds that 11,000 and 12,000 atmospheres would be the respective compressional forces for these liquids to satisfy the equation, whence for charcoal he obtains 58,000 atmospheres as the internal pressure.

This hypothesis of a compressional force of great magnitude on the surface of charcoal effecting a marked contraction in a relatively thick skin of liquid is open to serious criticism. We have noted already that in the case of vapours on solid surfaces the first unimolecular layer may be held very tenaciously whilst the subsequent layers when formed are held but loosely. Again, all available evidence seems to indicate that the surface of a film but a few hundred molecules thick at the most, would possess all the properties of a surface of the bulk liquid. It is unlikely that any serious change in the properties of the interface would occur in a transition from a solid-vapour to a solid-liquid system.

It is more than probable that these variations in the apparent densities of charcoals are to be ascribed to a difference in the depths of penetration of the liquids. Thus non-wetting liquids such as mercury would not readily penetrate the large macropores in the solid, far less into the micropores (below 100 Å. in diameter) which exist in charcoal. We should thus anticipate that when mercury is employed as immersion liquid the charcoal density would be but small. Actually a value of only 0·865 was obtained by Harkins and Ewing.

With pentane on the other hand penetration is almost complete even into the fine micropores and a density of 2·129 was actually obtained.

Howard and Hulett (*Jour. Phys. Chem.* Oct. 1924) brought forward additional evidence in favour of this hypothesis by determining the apparent densities of charcoals with helium gas in place of an immersion liquid with the following results:

Charcoal	Density
Coconut	2·12
Sugar	2·26
Graphite	2·28

The slight differences in these various forms of carbon are fully accounted for by the presence of impurities especially hydrogen and oxygen always present even in good outgassed carbon.

On immersion of even well outgassed charcoal in water we must imagine that many of the micropores are not filled with water and thus an apparent diminution of the density of the solid occurs. These micropores cannot of course be empty for otherwise there is no reason why the liquid wetting the sides of the tubes should not fill them. If the micropores still contain small traces of gases not removed by the process of outgassing these will be compressed into pockets at the ends of the blind tubes, the pressure in the case of a micropore of 100 Å. diameter would be about sixteen atmospheres.

An attempt has been made to decide between these two hypotheses advanced to explain the anomalous values obtained for density of charcoals by examining the density temperature curve for a system comprising water and charcoal. From a knowledge of

the coefficients of expansion of glass, graphite and water the density temperature curve on each side of the critical temperature of 4° C., at which water is most dense can be calculated. If in reality gas be present in the charcoal a marked alteration in the point of minimum density will be obtained, and, on the assumption that the gas behaves in an ideal manner the volume of the occluded gas may be determined from the slope of the density temperature curve. Preliminary experiments on charcoal of apparent density in water of 1·84 showed that gas was actually present in relatively large quantities. On correcting the observed density for the amount of gas present, calculated from the experimental data, a true density of 2·12 was obtained. The charcoal employed was sugar charcoal and it is by no means certain that the true density should not be somewhat greater than the corrected value obtained. Nevertheless the hypothesis of variable penetration of the immersion liquid receives additional if not unqualified support from these experiments.

Adsorption from Solutions.

6. Non-electrolytes.

If an aqueous solution of some colouring matter be agitated with powdered charcoal and a determination of the concentration of the colouring matter in the solution be made both before and after the operation, the solution will be found to be much less concentrated due to a selective removal of the colouring matter by the charcoal. Such selective removal is frequently termed positive adsorption.

As a rule the solutes which are positively adsorbed by solid adsorbents are negatively adsorbed at a gas-liquid interface. Such behaviour is in agreement with Antonow's rule that

$$\sigma_{a\ \text{vapour}} = \sigma_{b\ \text{vapour}} + \sigma_{ab},$$

where a and b are two phases in equilibrium (in his limited definition two mutually saturated liquids) of which a has the higher surface tension against vapour.

Now Antonow's rule appears to be valid for two liquids provided that "saturation" be carefully defined and it is true for solid and liquid interfaces provided that the angle of contact be zero.

Thus $\sigma_{\text{charcoal, water}} = \sigma_{c\text{ air}} \sim \sigma_{H_2O\text{ air}}$ ....(i),

$\sigma_{\text{charcoal, KCl solution}} = \sigma_{c\text{ air}} \sim \sigma_{KCl\text{ aq. air}}$ ....(ii).

Now $\sigma_{c\text{ air}} > \sigma_{H_2O\text{ air}}$ or $\sigma_{KCl\text{ aq. air}}$, otherwise charcoal would not adsorb water, so we may replace $\sim$ above by $-$.

From (i) and (ii) we obtain

$$\sigma_{c\text{ } H_2O} - \sigma_{c\text{ KCl aq.}} = \sigma_{KCl\text{ aq. air}} - \sigma_{H_2O\text{ air}} > 0,$$

so that whilst potassium chloride raises the surface tension of water-air it lowers the surface tension water-charcoal and is therefore positively adsorbed, at the interface.

It must however be pointed out that in the above deduction we have assumed $\sigma_{\text{charcoal, water}}$ is equivalent to $\sigma_{\text{charcoal saturated with water, water}}$ as demanded by Antonow's rule. There is probably a not inconsiderable difference between these values (cf. mercury saturated with organic vapours, p. 58). This difference may be used as a possible explanation of why some solutes in water are positively adsorbed both at an air and a charcoal interface.

This property of selective removal is utilised largely in industry and the following table from Bancroft indicates some of the more important decolourising agents together with their efficiencies in arbitrary values.

Material	Efficiency
Alumina... ...	100
Fuller's earth ...	50
Bauxite	50–30
Ignited peat ...	25
Bone charcoal ...	24
Bog iron ore ...	20
Fuller's earth II	17
Ferric oxide ...	17
Ball clay... ...	14
Fuller's earth III	10
China clay ...	3
Kieselguhr ...	3

The rate and completeness of removal is generally greater at high temperatures and is in general proportional to the fineness of the mesh; bauxite, for example, increases its efficiency from 100 for 40/60 mesh to 170 for a 60/80 mesh.

The property of adsorption from solutions of a particular solute is in general, apart from the fact that both solvent and solute are adsorbed (see p. 181), complicated by the fact that the adsorbing surface presented to the liquid is not uniform but broken up into a series of fissures or capillaries as is the case with solids such as charcoal and pumice or "gels" such as those of silica and alumina with the result that true equilibrium between solution and adsorbent may not result until after long periods of time, necessary for the intradiffusion of the solution into the absorbent during which period secondary chemical action may take place. For comparative purposes adsorption as distinguished from absorption or sorption (J. W. McBain, *Phil. Mag.* XVIII. 6, 1909) is considered to take place rapidly in solutions as well as in gases (see p. 123).

The early experimental data of Freundlich (*Kapillarchemie*) indicated that the adsorption of a solute from a solution followed the general laws governing the adsorption of vapours by solids, i.e. the Freundlich isotherm

$$x = KC^{\frac{1}{n}} \quad \text{or} \quad x^n = KC,$$

where x is the amount adsorbed per gm. of adsorbent, C the bulk concentration of the solute in equilibrium with the solid, n and K constants.

The values of the exponent n are found to vary in the most diverse manner, as is exemplified by the following:

Adsorbent	Solute	Solvent	n
*Silica	KCl	H_2O	1
†SnO_2	,,	,,	1
‡Charcoal... ...	,,	,,	1
§Cr_2O_3	Alizarine	,,	3
‖Cellulose ...	Methylene blue	,,	2
‖Silk	Indigo carmine	,,	2
Basic lanthanum acetate	I_2	,,	2
¶Starch	,,	,,	5

* Schmidt, *Zeit. Phys. Chem.* xv. 56, 1894.

† Van Bemmeln, *Zeit. anorg. Chem.* xxiii. 113, 1900.

‡ Lachs and Michaelis, *Zeit. anorg. Chem.* xvii. 2, 1911.

§ Georgievics, *Zeit. Farbenindustrie*, ii. 253, 1903.

‖ Biltz, *Ber.* xxxvii. 719, 1904.

¶ Küster, *Liebig Ann.* ccLxxxiii. 364, 1871.

In general however the values of the exponent n are not whole numbers but fractional as in the following cases:

Adsorbent	Solute	Solvent	n
Silk ...	Picric acid	H_2O	2·88*
		C_2H_5OH	2·75*
Charcoal...	Acetic acid	H_2O	2·35†
		C_6H_6	2·40†

* Appleyard and Walker, *J.C.S.* LXIX. 1334, 1896.
† Freundlich, *Kapillarchemie.*

7. Adsorption of solvent and solute.

The adsorption of a particular solute from a solution is however dependent upon the nature of the solvent, a point not envisaged by the Freundlich isotherm. The influence of the solvent on the amount of adsorption of a particular solute has been investigated in the case of iodine and charcoal by Davis (*J.C.S.* XCI. 1666, 1911) who found that the amount of iodine adsorbed by charcoal from solutions of equimolecular concentrations decreased with the nature of the solvent in the following order:

Blood charcoal ... CCl_3H, C_2H_5OH, $CH_3COOC_2H_5$, C_6H_6, $C_6H_5CH_3$,
Sugar charcoal ... CCl_3H, $C_6H_5CH_3$, $CH_3COOC_2H_5$, C_6H_6, C_2H_5OH.

Although in part this order may be affected by subsequent reaction of the iodine with the organic solvent under the influence of catalytic material in the charcoal (Schmidt, *Zeit. Kolloid. Chem.* XIV. 242, 1914) yet similar alterations have been noted by Freundlich (*ibid.* p. 260) with other solutes, e.g. benzoic and picric acids, who found the following order for decreasing adsorption for benzoic acid: water, benzene, ethyl ether, acetone: for picric acid, water, ethyl, alcohol, benzene.

That the solvent plays an important part in the adsorption process is evident from the various cases of "negative" adsorption (Gore, *Chem. News*, LXIX. 23, 1894; Lagergren, *Bihang till k. Svenska Vet. Akad. Handl.* II. 244; Trouton, *B.A. Reports*, 328, 1911; Gustafson, *Zeit. Phys. Chem.* XCI. 385, 1916) in which a solution shaken up with the adsorbing agent has apparently

increased in concentration instead of decreasing as would be anticipated.

Williams (*Trans. Farad. Soc.* I. 1914) has shown that on the assumption that both solvent and solute are adsorbed by the adsorbing agent we may obtain "positive," "zero" or "negative" adsorption as the solute is adsorbed more strongly, equally or less strongly than the solvent and that as an alteration in concentration of the solution takes place the adsorption may pass through all these separate phases.

If we denote by u and w the amount in grams of solute and solvent adsorbed per gram adsorbent when in equilibrium with a solution containing c grams of solute per gram of solute, we find that the excess of solute per gram adsorbent, generally called the amount adsorbed u_0, given by

$$u_0 = u - w\frac{c}{1-c}\,.$$

If in dilute solution when c is small the true adsorption u is proportional to concentration or $u = kc$ we obtain

$$u_0 = u - wc = (k - w)\,c,$$

or

$$u_0 = k'c,$$

where k' may be either positive or negative. Whilst in concentrated solution where c is nearly unity we have a relationship of a similar type

$$w = k'(1-c),$$

or

$$w_0 = (k' - v)(1-c),$$

or

$$u_0 = u - \frac{w}{1-c} = u - k'.$$

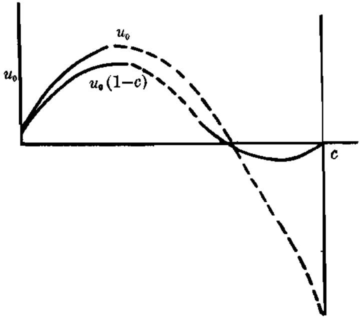
If w_0 is positive near $c=1$ as u_0 is generally positive near $c=0$ it follows that near $c=1$ u_0 will be negative, hence the c, u_0 and $c, u_0(1-c)$ curves will be of the type shown on p. 182.

Or, in general, positive adsorption rising to a maximum will be followed by zero and eventually negative adsorption, due to the fact that solvent and solute are both adsorbed.

In a few cases examined Williams has actually obtained this transition as instanced by the following data for the adsorption of potassium chloride in aqueous solution by charcoal.

c	u_0
·00044	+ ·00032
·00616	+ ·00230
·02050	+ ·00250
·05630	+ ·00170
·06800	− ·00170
·12800	− ·00260
·17000	− ·00770

Similar results were obtained with magnesium sulphate; whilst with ammonium chloride a maximum was found, this was not followed by negative adsorption over the concentration range examined.



Osaka (*Mem. Coll. Sci. Kyoto Univ.* VI. 257, 1915) has obtained positive adsorption in the case of sodium and potassium nitrates and for potassium bromide and iodide, and negative adsorption in the case of sodium and potassium sulphate as well as potassium iodide.

Gustafson (*Zeit. Physik. Chem.* CXI. 405, 1916) has attempted to extend the conception of Williams that solvent and solute are both adsorbed with the aid of the Freundlich isotherm in the following way.

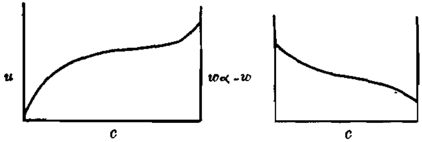
In general there will be u grams of solute and w grams of solvent adsorbed per gram of adsorbing agent. If u_∞ and w_∞ be the respective

amounts adsorbed in pure solvent and solute respectively Gustafson finds in the case of aqueous acetic acid and charcoal that

$$u = kc^{\frac{1}{n}}$$

and $$w_\infty - w = k'c^{\frac{1}{n'}},$$

and the dual adsorption can be represented by two curves.



Williams (*Meddel. från vet. Akad. Nobelinstitut,* II. 21, 1913) on the other hand has found that a more general relationship of the type

$$\frac{u}{u_\infty} + \frac{w}{w_\infty} = 1$$

gives a fair approximation to the experimental data.

The direct determination of the amount of solvent adsorbed by an adsorbing agent is a matter of some difficulty. The most general method suggested by Arrhenius (see Williams, *loc. cit.*; Osaka, *Mem. Coll. Sci. Kyoto*, VI. 257, 1915) is to leave the dry adsorbent in a desiccator exposed to the vapour of the pure solvent or solution containing a non-volatile solute. The method is open to two serious defects. As instanced by the experiments of Davis the adsorption of a solute is affected by the simultaneous adsorption of the solvent. Thus there is no justification for the assumption that the amount of, say, water adsorbed by charcoal exposed to water vapour above a certain concentrated solution of sodium chloride will be identical with the amount of water adsorbed by the charcoal if immersed in that solution. Again if sufficient length of time be given for the exposed charcoal to attain equilibrium with the vapour the water vapour will enter the pores and capillaries of the charcoal and condense thus yielding too high values for the adsorbed water. Bakr and King (*J.C.S.* CXIX. 456, 1921) have attempted to obviate these difficulties in the case where both solvent and solute are

volatile by maintaining the adsorbing agent at a higher temperature than the liquid with which it is desired to attain equilibrium. A fair agreement was obtained between the amounts adsorbed by charcoal by distilling benzene from the liquid to the charcoal on the one hand and hy the reverse process vaporising the excess benzene from a moist charcoal to the liquid. A knowledge of the composition of the adsorbed two dimensional phase which is in equilibrium with a three dimensional phase, the liquid of known composition, would together with information on the molecular diameters of the constituents in the adsorbed phase give us a direct method for evaluating the specific surface of the adsorhing material.

In some cases it has been found that the maximum or saturation adsorption of a solute from a solution corresponds to the formation of an adsorption layer one molecule thick. Thus Euler (*Zeit. Elektrochem.* XXVIII. 446, 1922) found that a maximum adsorption of silver ions by silver and gold leaf was attained in a 0·03 N solution. It was found that 5·5 and 8·5 to 9 mgm. of silver ions were adsorbed hy a square metre of metallic silver and gold respectively, such a surface concentration is practically unimolecular. The adsorption of silver ions by silver bromide (K. Fajans, *Zeit. Phys. Chem.* CV. 255, 1923) was found on the other hand to be not complete, for only every fourth bromide ion in a silver bromide surface was found to adsorb a silver ion. Similar conclusions as to the unimolecular character of the adsorbed film in the case of chemical charcoal as an adsorbing agent for fatty and amino acids may be drawn from the data of Foder and Schonfeld (*Koll. Zeit.* XXXI. 75, 1922).

Odén (*Nova Acta Reg. Soc. Upsala,* III. 4, 1913) showed that the maximum adsorption of sodium chloride by sulphur particles 1000 Å. in diameter yielded a value of 2·79 gms. NaCl for 100 gms. of the sulphur. If the density of colloidal sulphur be taken as $\Delta = 2$ we find that one sulphur particle of area 3×10^{-10} sq. cm. adsorbs 3×10^{5} molecules giving on the assumption of an unimolecular layer a mean area for the sulphur molecule of 10^{-15} sq. cm. or 10 Å. which is a close approximation to the value calculated in other ways.

Euler and Zimmerlund (*Archiv f. Kem. miner. u. geol.* VII. 31, 1920 and VIII. 14, 1921) found that mercury droplets adsorbed

from a three-quarter saturation solution of mercurous chloride sufficient salt to effect a 25 % saturation of the surface.

The conclusions of Paneth and Radu (see ante p. 173) on the unimolecular character of the film of the readily adsorbable dyes on charcoal surfaces have already been observed.

8. The Adsorption of Ions.

Investigations on the adsorption of a series of salts possessing common anions or cations have shown that the adsorption of an ionising salt is an additive property of the cation and anion, thus the order of the adsorption of a series of sodium salts of various acids is identical with the order for the potassium or ammonium salts. With charcoal as adsorbing agent Michaelis and his co-workers (Lachs and Michaelis, *Koll. Zeit.* IX. 275, 1911; Rona and Michaelis, *Biochem. Zeit.* XCIV. 240, 1919; XCVII. 85, 103, 1920 and Hartleben, *Biochem. Zeit.* CXV. 46, 1921) have found the following series for cations and anions in decreasing adsorptive power.

CATIONS.

Organic colour bases:

$H^{\cdot}$, $Ag^{\cdot}$, $Hg^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, $NH_4^{\cdot}$, $K^{\cdot}$, $Na^{\cdot}$

ANIONS.

Organic colour acids:

OH', CN', S'', I', NO_3', Br', Cl', HPO_4'', SO_4''

(See also Morawitz, *Kolloid Chem. Beihefte*, I. 301, 1910.)

In all cases comparisons were made with dilutions electrically equivalent, *e.g.* $0{\cdot}1N$ NaCl, $0{\cdot}05N$ $MgCl_2$, $0{\cdot}033N$ $AlCl_3$.

It will be noted that with the exception of the organic cations and anions the more mobile hydrogen and hydroxyl ions are most readily adsorbed, whilst in the case of the metallic ions the influence primarily of the valency of the ion and both the position of the metal in the electrolytic potential series as well as the ionic mobility is most marked, the higher the valency and the more noble the element the more readily it is adsorbed.

With charcoal as adsorbing agent in the case of an acid such as hydrochloric acid the hydrogen ions are more readily adsorbed than

the chlorine ions; expressed in terms of the Freundlich isotherm we obtain two independent equations

$$x_{\dot{H}} = a\,[\dot{H}]^{\frac{1}{n}},$$

$$x_{Cl'} = a'\,[Cl']^{\frac{1}{m}},$$

where in general $a \neq a'$ and $\frac{1}{n} \neq \frac{1}{m}$.

The selective adsorption of the hydrogen ions cannot proceed to true equilibrium owing to the electrostatic attraction between the dissimilar ions, consequently chlorine ions are adsorbed in excess of their equilibrium concentration and since the hydrogen ions on adsorption have to do work in increasing the surface concentration of chlorine ions above their proper value, the true adsorption value of the hydrogen ions is not attained.

On the addition of a neutral chloride to the solution the chlorine ion concentration is increased, and provided that the cation of the added chloride does not affect the adsorption of the hydrogen ion, i.e. on addition of a weakly adsorbed cation, such as potassium, the adsorption of the hydrogen ion can now proceed to its normal equilibrium value without having to retain any adsorbed chlorine ions by electrostatic attraction. The addition of potassium chloride to a hydrochloric acid solution will thus augment tbe adsorption of the acid by the charcoal, a result confirmed by Michaelis and Rona.

Identical maximal values for the adsorption by blood charcoal were found for the acids HCl, HNO_3, H_2SO_4 in the presence of their neutral salts, viz. a 45 °/₀ adsorption in a 0·01 molar solution. Of interest is the fact that similar results were obtained for the adsorption of hydroxyl ions, e.g. caustic potash and soda, in the presence of excess potassium and sodium chlorides, both hydrogen and hydroxyl ions exhibiting equal adsorption.

9. Adsorption with active adsorbing agents.

Pure charcoal adsorbs hydrogen and hydroxyl ions with equal facility and is itself inert in that it discharges no ions into the solution. Many adsorbing agents, however, are either acid or basic in character in that they can discharge either hydrogen ions, e.g.

silicic acid or hydroxyl or other anions, e.g. ferric hydroxide into the solution. Under these conditions adsorption and ionic interchange may take place; thus the silicates adsorb methylene blue hydrochloride, but an equivalent of calcium ions replaces the methylene blue in the solution according to the equation

calcium silicate + methylene blue HCl → methylene blue silicate + calcium chloride.

If ferric hydroxide be prepared by the hydrolysis of ferric chloride the resulting colloid contains chlorine ions which can be replaced by more readily adsorbable picrate or eosinate ions leaving hydrochloric acid in solution.

On shaking Fuller's earth with neutral sodium chloride solution the solution is found to become distinctly acid to litmus, an indication that the sodium ions in the solution adsorbed by the Fuller's earth have been replaced by hydrogen ions from the earth, according to Michaelis not directly as such but by resulting from the liberation of calcium ions, the calcium chloride formed then undergoing hydrolysis.

Bancroft (p. 121) advances an alternative explanation to the hypothesis of ionic interchange.

If a salt undergo hydrolysis in solution according to the equation

$$M^{\cdot} + X' + H_2O \rightleftarrows M^{\cdot} + OH' + X' + H^{\cdot},$$

and the adsorbing agent selectively adsorbs the acid $H^{\cdot}X'$ the hydrolysis will evidently proceed further until equilibrium is attained. In the case of Fuller's earth it may be considered that the earth selectively adsorbs hydrochloric acid leaving an alkaline *solution of caustic soda. This view of promoted hydrolysis by ad*sorption is at variance with the hypothesis of ionic interchange and can only be tested by careful analysis of the solution to find out whether ionic interchange has taken place or no.

Michaelis and Rona (*loc. cit.*) have concluded from an examination of various cases of adsorption, e.g. methylene blue hydrochloride by kaolin and by cellulose and of picric acid by iron hydroxide, that the mechanism is one of ionic interchange and not of promoted hydrolysis.

Bartell and Miller (*J.A.C.S.* XLVI. 1866, 1922, LXV. 1106, 1923) on the other hand in their investigations on the adsorption by clean

sugar charcoal of acid and basic dyes, such as methylene blue hydrochloride and sodium picrate and eosinate, showed that hydrolytic adsorption actually occurred. Thus in the adsorption of methylene blue hydrochloride at low concentrations both the colour base and the hydrochloric acid set free is adsorbed; as the concentration rises the colour base is preferentially adsorbed and the solution is left acid. The distinction is of importance in various operations of dyeing.

10. Surface reactions at the solid-liquid interface. The equilibrium of crystals in solution.

The fact that not only may the different surfaces of a crystal have different surface energies due to an alteration in the closeness of the packing of the molecules on the planes but also that the molecules at the corners and edges of a crystal cannot adhere so strongly as those in the interior of the plane surfaces give us, as Gibbs (*Scientific Papers*, p. 325) has pointed out, a great deal of information on the mechanism of solution and growth of small crystals.

When a crystal is in equilibrium with its saturated solution there must be a kinetic fluctuation between the molecules of the crystal and those of the circumambient solution. The conditions of equilibrium at such an interface have been considered from a statistical point of view by J. A. Butler (*Trans. Faraday Soc.* XIX. 659, 1924) on the following lines. A molecule passing outwards from the surface of the crystal experiences first an attraction towards the surface and after a certain point an attraction into the liquid; there thus exists a balance point at which the two opposing attractions are equal. If a surface of a crystal containing N molecules per sq. cm. be placed in contact with a solution containing N_s molecules per c.c. and we consider a slice of solution at the surface of the solid in thickness equal to the mean free path of solute molecules in the solution and containing N_1 molecules, then the number of molecules moving towards the surface with a kinetic energy E per gram molecule at any instant is according to Maxwell

$$\phi = \frac{N'}{\sqrt{\pi}} \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} d\sqrt{\frac{E}{RT}}.$$

The number of molecules escaping per second is equal to this quantity multiplied by the mean collision frequency, that is the mean velocity $\bar{v}$ divided by the mean free path $\bar{s}$. But $N_1 = N_s \bar{s}$, hence the number of solute molecules reaching the surface per second is

$$\theta = \frac{\phi \bar{v}}{\bar{s}} = \frac{N_s}{\sqrt{\pi}} \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} v d\sqrt{\frac{E}{RT}}$$

or $\theta = N_s A \sqrt{T} e^{-\frac{\lambda}{RT}}$, where $A = \sqrt{\frac{R}{2\pi M}}$.

If in reaching the balance point from the interior of the solute a molecule does work W_1 then the number of molecules reaching the balance point from the solution per second is

$$\theta' = N_s A \sqrt{T} e^{-\frac{W_1}{RT}}.$$

The molecules at the surface of a crystal move only in a vibrational manner about an equilibrium position perpendicular to the crystal surface; the number escaping per second will evidently be proportional to (*a*) the number on the surface layer, (*b*) the number having at any instant a kinetic energy greater than λ per gram molecule, and (*c*) the number of times on an average the outward movement is repeated per second (assuming that the normal distribution of energy among the surface molecules is attained afresh for each new outward movement). That is we replace the mean collision frequency by the vibration frequency ν and obtain

$$\theta = \frac{N}{\sqrt{\pi}} \nu \int_{E=\lambda}^{E=\infty} e^{-\frac{E}{RT}} d\sqrt{\frac{E}{RT}}.$$

On integration

$$\theta = N\nu \sqrt{\frac{RT}{\lambda\pi}} e^{-\frac{\lambda}{RT}} \left\{1 - \frac{RT}{2\lambda} + \frac{3R^2T^2}{4\lambda^2} \cdots\right\},$$

where if λ is very considerably greater than $\frac{RT}{2}$, this reduces to

$$\theta = N\nu \sqrt{\frac{RT}{\lambda\pi}} e^{-\frac{\lambda}{RT}}.$$

If in reaching the balance point a molecule from the surface layer does work W_2 per gram molecule, then the number of molecules reaching the balance point from the surface per second is

$$\theta'' = NA' \sqrt{T} e^{-\frac{W_2}{RT}}, \quad \text{where} \quad A' = \nu \sqrt{\frac{R}{W_2 \pi}}.$$

In a saturated solution equilibrium between solution and deposition exists, or

$$\theta' = \theta''$$

or
$$NA' \sqrt{T} e^{-\frac{W_2}{TR}} = N_s A \sqrt{T} e^{-\frac{W_1}{RT}}.$$

Writing $C = \frac{N_s}{N_0} \times 1000$, where $N_0 =$ the Avogadro number

$$\log_e C = \frac{W_1 - W_2}{RT} - \log_e \frac{AN_0}{1000A'N}$$

or
$$\log_e C = \frac{W_1 - W_2}{RT} - \log_e \frac{N_0}{1000\,N} \sqrt{\frac{W_2}{2M\nu^2}}.$$

$W_2 - W_1$ is evidently the heat of solution at saturation.

Since the edge molecules are held less tenaciously than those in the middle of the planes we must suppose that at equilibrium several of the outermost layers of the molecules on the sides of crystal surfaces are incomplete toward the edges. This fluctuation is less as we proceed away from the edge towards the centre of the plane surface. To produce continued growth of a crystal it is necessary to build up the molecular planes at the surface. There is however a great difficulty in commencing a fresb plane since until a molecular layer is formed the single molecules adhere to the underlying plane less tenaciously than those forming part of the underlying plane (in true equilibrium with the liquid). It necessarily follows that a certain small but finite degree of super-saturation is necessary to permit a crystal to grow.

The difference between the minimum growing concentration and the saturation equilibrium value represents the difference in the adherence of a molecule in a plane and one adhering to the plane surface.

For solution on the other hand no such difficulties occur. It has already been noted that the edges of the planes are already stripped under conditions of equilibrium; a small decrease in the concentration of the solution simply extends the edges further towards the centre of the plane until it is stripped entirely. The mechanism of crystal growth thus presupposes a finite degree of super-saturation, this no doubt varies with the surface energies of the crystal faces and will probably be greatest for the surfaces for which σ_{sl} is least,

whilst on solution of a crystal the degree of under-saturation necessary to produce a continued stripping of the surface will also be least for surfaces of low σ value. We thus arrive at the conclusion of Gibbs: "The effect of dissolving a crystal is therefore to produce a form which probably differs from that of theoretical equilibrium in a direction opposite to that of a growing crystal."

In actual processes of crystal formation and solution, forces other than surface forces may play an important part, thus in the solution of crystals it is necessary to dissipate the heat evolved on solution (see Nacken, *Neues Jahrbuch Min. Geol. Pal.* II. 133, 1915). Such dissipation may take place most readily at edges and corners. Again a crystal undergoing solution in a nearly saturated solution will be surrounded by a saturated layer of solution. This layer being denser than the surrounding medium will sink to the bottom of the vessel and thus accelerate the normal process of solution. In this way also exposed edges may dissolve more rapidly than the plane surfaces.

11. Solution at plane surfaces.

The rate of solution of solids in liquids is found to be a reaction of zero order provided that the concentration of the solution remains unchanged and the surface exposed to solution constant, as is indicated by the early experiments of Wenzel (*Lehre der Verwandtschaft,* XXVIII. 1777) and of Veley (*J.C.S.* LV. 361, 1889; *Phil. Mag.* CLXXXII. 279, 1891) on the rate of solution of metals in acids.

In the case of solution of a solid in a limited volume of solution the rate of solution will follow a unimolecular law, thus in the case of metals dissolving in acids, or salts in water, for a constant area of interface the rate will be expressed by the equation

$$\frac{dx}{dt} = k(a - x),$$

where a is the original concentration of the acid, a conclusion confirmed by Spring's experiments on the rate of solution of calcspar in hydrochloric acid. The rate of solution of solids has been examined in detail by Noyes and Whitney (*Zeit. Phys. Chem.* XXIII. 689, 1897), Nernst (*ibid.* XLVII. 52, 1904), Brunner (*ibid.* XLVII. 56, 1904), Nernst and Merriam (*ibid.* LIII. 235, 1905) and others.

It was found that the solution of a solid consists essentially of two processes, the actual process of interaction of solid and solvent and the diffusion of the solvated solute away from the surface.

The crystal surface may be regarded as covered with a layer of saturated solution of a definite thickness through which the products have to diffuse. If the actual solvation of the solid proceeds rapidly in comparison to the process of diffusion the rate of solution will be essentially that of diffusion, and can accordingly be expressed by the Fick diffusion equation, the rate of solution per unit area of interface being given by

$$-\frac{dx}{dt} = D\,\frac{C_s - C}{\delta}$$

where D is the diffusion constant, C_s the saturated, C the actual concentration of the solution and δ the thickness of the diffusion layer. Experimental evidence in support of this point of view as to the mechanism of the process has been advanced by examination of the rates of solution of such substances as benzoic acid, lead chloride and silver acetate in water; also by the solution of magnesia in acetic, benzoic and hydrochloric acids. As examples may be cited the following values for the solution rate of small rods of magnesia rotating at a constant speed in the solvent:

Solvent	Velocity constant k	Diffusion coefficient
Benzoic acid ...	1·55	0·75
Acetic acid ...	2·05	0·95
HCl and $MgCl_2$	8·10	6·70

The velocities of solution are evidently approximately proportional to the diffusivity and not to the acid strengths. The temperature coefficient of these processes is likewise small being 1·25 for a rise of 10° C. of the same order as that for diffusion.

The values of δ the film thickness are found to vary with the nature of the reaction, but lie within the limits 0·02 to 0·065 mm. The film thickness is dependent on the speed of rotation n for the case of the solution of benzoic acid and of magnesium benzoate in water.

We may likewise obtain an estimate of the thickness of the adsorbed film by determining the maximum current density at which ions may be deposited at an electrode which is kept in rapid rotation. The ions being deposited must be regarded as migrating across a film of thickness δ from a concentration equal to that in the bulk of the electrolyte to a region of zero concentration under the applied electromotive force. Thus Ackerberg (*Zeit. Anorg. Chem.* XXXI. 161, 1902) obtained $\delta = \cdot 095$ mm. from measurements on the rate of the electrolytic oxidation of oxalic acid. Fischer (*Elektrochemie,* p. 60) obtained the following values from data on the limiting current densities in the precipitation of copper at a rotating cathode:

n R.P.M.	δ in mm.
250	·0635
800	·0565
1100	·0510

Dushman (*Jour. Phys. Chem.* XIV. 885, 1910) found $\delta = \cdot 040$ mm. under similar conditions, whilst Brunner (*loc. cit.*) found that $\delta n^{\frac{2}{3}}$ was approximately constant.

The catalytic decomposition of hydrogen peroxide at the surface of platinum foil investigated by Bredig and Tetelow (*Zeit. Elektrochem.* XII. 581, 1906) was found to obey a unimolecular law and the seat of the reaction was shown to be the thin saturated layer at the surface of the metal.

In some cases, e.g. the oxidation of hydrocarbons by potassium permanganate (Meyer and Saam, *Ber.* XXX. 1935, 1897), the hydrolysis of emulsions of esters in water (Goldschmidt, *Zeit. Phys. Chem.* XXXI. 235, 1899), and the dissolution of arsenious oxide (Drucker, *Zeit. Phys. Chem.* XXXVI. 693, 1901), the actual chemical reaction between solvent and solute appears to be slower than the process of diffusion, and thus the rate of chemical action is independent of the diffusion coefficient.

The observations of Goldschmidt on the hydrolysis of esters are in contradiction to the data obtained by Norris and McBain (*J.C.S.* CXXI. 1362, 1922) who obtained the normal temperature coefficient of 1·5 and the $\delta n^{\frac{2}{3}}$ relationship for the saponification of oils and fats by aqueous alkali.

12. Crystallisation from solution.

In the rate of crystallisation of a substance from a supersaturated solution two independent factors have to be considered, firstly the rate of nucleus formation from which crystallisation may proceed and secondly the rate of growth of a nucleus once it is formed.

Nucleus formation.

As has already been noted (p. 167) the solubility of small crystals is greater than that of large ones, hence before a nucleus can act as a centre from which spontaneous crystallisation may proceed it must possess a certain limiting size dependent on the surface energy of the solid and the degree of supersaturation of the solution. The spontaneous formation of such a nucleus can only take place in solution as the result of intermolecular collision. Adopting Langmuir's hypothesis of inelastic collision each contact between two molecules of solute in a solution results in an adhesion for a definite although short period of time, the periods being in all probability somewhat longer than in the case of gases. In general the problem of adherence on collision in solution is complicated by the fact that both ions of electrolytes and molecules of non-electrolytes are solvated, and thus do not actually come in contact with one another. For orientated collision to take place so as to build up the elementary crystal lattice it is necessary to postulate either contact between unsolvated molecules or ions, or a movement of the solute particles towards one another within their solvated atmospheres which then merge into a common sheath. In the rapid condensation of metallic vapours it has likewise been noted (see p. 124) that adherence may result in the formation of an amorphous material which sinters to the crystalline state at a rate dependent on the mobility of the atoms within the mass. A somewhat similar phenomenon has been observed and investigated by von Weimarn (see p. 204) in the preparation of colloids from highly supersaturated solutions. The rate of formation of nuclei will however in general increase with increasing concentration of the solution. At any definite temperature the molecules are in thermal agitation by which intermolecular contacts are produced; at the same time the same agitation is the operative process by which rupture is caused between adhering molecules. Thus there will be a maximum

rate of nucleus formation at a definite temperature; below which temperature the rate of intermolecular collision is decreased by the decrease in the thermal agitation of the molecules and the increase in the viscosity of the medium; eventual solidification to glasses taking place. Above this temperature, in spite of the increase in the rate of collision, the rate of disintegration of the micro-nucleus is increased.

The existence of such a maximum has been shown for a number of solutions by Tammann (*Kristallisieren und Schmelzen*, p. 151).

13. Rate of crystallisation.

If a crystal surface be exposed to a supersaturated solution the surface will commence to grow. As has already been noted the surface energy of a crystal is dependent not only on the nature of the substance but also on the packing in the space lattice, the rate of growth will thus vary with the crystal face, e.g. the faces of a crystal of the cubic class will possess different growth rates depending on whether the 1, 0, 0 or 1, 1, 1 face is exposed to the solution.

It was noted in the case of solution that in many cases the rate of solution was apparently governed by the rate of diffusion of the solute through a saturated film of definite thickness. As a first approximation the growth of a crystal may be regarded as an analogous process, viz. the diffusion of the salt from a supersaturated solution through a saturated film to the crystal surface. Under these conditions the growth rate per sq. cm. would be given by the expression

$$-\frac{dx}{dt}=\frac{D}{\delta}(C_0-C_s),$$

where C_0 is the concentration of the supersaturated solution, C_s that of the saturated film.

The velocity of linear crystallisation has been determined in the case of fused solids by Tammann and his co-workers (*loc. cit.*), in supersaturated solutions by Marc (*Zeit. Phys. Chem.* LXI. 385, 1908, LXVII. 470, 1909, LXVIII. 104, 1909, LXXIII. 685, 1910, LXXV. 710 1911, LXXIX. 71, 1912), Le Blanc (*ibid.* LXXVII. 614, 1911), and others.

The crystal growth rate has been found in many cases to be extremely rapid, more rapid than can be accounted for on the diffusion hypothesis; thus Tammann (*loc. cit.*) found for benzophenone a maximum crystallisation velocity of 2·4 mm. per minute (Walton and Judd, *J. Phys. Chem.* XVIII. 722, 1914). Much higher values, e.g. 6840 mm. per minute for water and 60,000 mm. per minute for phosphorus (Gernez, *C.R.* XCV. 1278, 1882) have been recorded. In some cases the rate was found independent of the speed of rotation of the stirrer and occasionally the reaction velocity followed a bimolecular law instead of the simple unimolecular expression which holds true for solution.

14. Influence of addition agents on rates of solution and crystallisation.

The rate of solution of crystals of potassium sulphate was found to be uninfluenced by the addition of many substances such as quinoline yellow to the solution by Marc and Wenk (*Zeit. Phys. Chem.* LXVIII. 112, 1910). Small alterations in the solution rates are however to be expected on the diffusion hypothesis if the extraneous material or "addition agent" affects the diffusion constant of the salt in the solution. Friend and Vallance (*J.C.S.* CXXI. 466, 1922) have shown a slight retardation in the rates of solution of potassium sulphate in solutions containing small amounts of agar and gelatine. The rates of solution of metals such as iron in acids is much retarded by the addition of many substances such as gelatine and agar (Friend and Dennet, Friend and Vallance) as is exemplified by the following figures for the retardation caused by the addition of small quantities of gum acacia added to normal hydrochloric acid in the solution of iron:

Gum acacia % added	Retardation %
0	0
0·001	0
0·01	40·8
0·05	45·1
0·10	60·4
0·20	62·5
0·50	70·8

The dilutions are too great to alter sensibly the diffusion constant of the medium, Friend suggests that the extraneous material or addition agent is selectively adsorbed and thus protects the iron from attack. An alternative explanation is the formation of an insoluble compound on the metal surface such as obtains in many cases of passivity.

In the converse case of crystallisation from a fused material or from a supersaturated solution the influence of addition agents is most marked. No regularity has been observed in the influence of soluble impurities on the formation of nuclei (Tammann, *loc. cit.*), the effect of the addition of powdered solids which occasionally act as nuclei has likewise not proved amenable to systematic classification although the criteria of isomorphism, e.g. identity or close approximation to identity in crystalline form, or the formation of mixed crystals hold true in cases where the supercooling is not great.

The effect of extraneous material on the linear velocity of propagation of crystal growth is marked and definite.

V. Pickardt (*Zeit. Phys. Chem.* XLII. 17, 1902) in his investigations on the lowering of the crystallisation velocity of fused benzophenone in the presence of various substances came to the conclusion that equimolecular proportions of the addition agents produced an identical lowering. According to Freundlich (*Kapillarchemie*, p. 448) this relationship only holds true for substances which possess identical constants in the Freundlich isotherm, the lowering of the velocity being due to adsorption of the addition agent on the crystal surface and is not occasioned by an alteration in the possible variables D or δ.

Similar observations in the retardation of crystallisation from solutions of salts such as potassium sulphate have been made by Marc, who showed that the retardation was most marked in the presence of dyes, such as quinoline yellow which were strongly adsorbed by the crystals. In the electro deposition of metals in the presence of addition agents these materials can be detected in the electrolytically deposited metal.

The effect of such addition agents, which are strongly adsorbed, is in general not limited to an alteration in the velocity of crystalline growth, but frequently affects the crystal habit. The adsorbed material lowers the interfacial surface energy of the crystal and

thus may permit the growth of those facets which normally possess too much interfacial energy to come into existence, e.g. octahedral crystals from sodium chloride in the presence of urea (Spangenberg, *Zeit. Kryst.* LXI. 189, 1925), dendrites from silver chloride in the presence of methylene blue, fine grained metal from the electrolysis of lead solutions in the presence of small quantities of gelatine and dendrites in the presence of relatively high concentrations (see Marc, *loc. cit.*, Reinders, *Zeit. Phys. Chem.* LXXVII. 680, 1911).

A few cases have been recorded (Dreyer, *Zeit. Phys. Chem.* XLVIII. 487, 1904) where the effect of the addition agent on the crystallisation velocity is to be attributed to an alteration in the diffusion constant of the solute in the solution, thus the velocity of crystallisation of formanilide is increased and not decreased by the addition of methyl or ethyl alcohol to the fused salt.

15. The formation of suspensions.

The effect of dispersing a solid in a liquid is to produce a solid disperse phase in a liquid dispersion medium. Such colloidal systems are termed "sols" dispersoids, suspensoids or suspensions. Suspensions may be produced by condensation from soluble salts in solution or by the disintegration or dispersion of a massive solid phase. By these methods it is possible to prepare colloidal systems consisting of a solid dispersed in a medium to any requisite degree of concentration and dispersity. Such disperse systems will not however necessarily be stable when thus prepared and in order to obtain stable systems factors other than mere size which controls the magnitude of the thermal or Brownian agitation have to be considered. Most potent amongst these stabilising factors which form an important part of investigations in systematic colloid chemistry are the electrical charges on the dispersed particles produced in general by ionic reactions occurring at the surface of the dispersed material and the circumambient liquid. We find also that extraneous materials which are preferentially adsorbed at the solid-liquid interfaces and lower the interfacial surface tension exert a great influence on the stability of the suspension. The mechanism and influence of these factors on the stability of suspensions will be discussed later (Ch. VII) and we will here confine

our attention to the general methods of procuring suspensions or disperse systems without special regard to their ultimate stability.

16. Methods of dispersion.

The formation of a colloidal suspension by the disintegration of a solid or the reforming of a stable colloidal solution from one in which the original suspension has undergone precipitation or agglomeration is frequently termed peptisation, a word introduced by Graham. This method of producing suspensions has been investigated in detail by Bancroft (*Second Report on Colloid Chemistry*, 1918) where he adopts Freundlich's interpretation of the mechanism of the process. On the adsorption of a liquid by a solid the surface energy of the solid is lowered and we may, according to Freundlich, regard the adsorbed film as one possessing a low surface tension on the liquid side and a high one on the other side; the adsorbed film will thus tend to disintegrate or peptise the solid substance. It is somewhat difficult to conceive of a film with a high and low surface tension on each side of it unless assumptions are made as to the thickness of the film. The process of disintegration of a solid may be regarded equally conveniently from a somewhat different point of view. That a crystal of a soluble salt dissolves in water may be considered as a demonstration that the cohesion between the molecules in the crystal is less than the adhesion of the water to the molecules constituting the surface of the crystal. As the quantity of salt in the water increases the adhesional forces between the salt water and crystal decrease until they become comparable with the intermolecular cohesion. Thus in strong solutions of electrolytes the formation of associated molecules, e.g. $(NaCl)_x$ $(BaCl_2)_y$, is by no means infrequent. In all those cases where the intermolecular forces holding the solid are sufficiently small or the adhesional forces between dispersion liquid and solid sufficiently great solution will take place. If the adhesional forces are but slightly greater than the cohesional forces, solution will not be complete but associated molecules or colloidal suspensions will be formed. Frequently mechanical methods of dispersion may be adopted and the resulting disperse phase "protected" from recoalescence by adsorption of a "protective" agent present in the solution.

The simplest cases of disintegration to a colloidal solution are those produced by immersion of a solid in a liquid, e.g. the disintegration of nitrocelluloses by means of amyl acetate. The solvent action of the medium is frequently greater at high temperatures than at low as noted by Lorenz in the dispersion of metals in contact with fused salts.

Bancroft cites cases in which disintegration is effected more readily in mixed solvents than by either solvent alone such as cellulose nitrate in ether alcohol mixtures. The interfacial surface tensions of such mixtures do not appear to have been measured.

Direct disintegration of ordinary chemical precipitates in water should be brought about by the addition of a solute which will be positively adsorbed by the precipitate in the solution. Such cases of positive adsorption should result in disintegration unless the cohesion of the precipitate be too great. No such cases of the addition of a non-electrolyte to water in effecting disintegration have been recorded although the addition of certain substances such as sugar and glycerine prevent the precipitation of certain hydrous oxides such as ferrous hydroxide where it is to be presumed that the internal cohesion is not great.

Not only may soluble non-electrolytes in a solution be adsorbed selectively by the material undergoing peptisation but frequently the adsorption of hydrated colloidal materials may take place. Although it can readily be demonstrated that substances like gelatine are adsorbed by and protect metals (and that they readily effect the disintegration of precipitates) yet no direct dispersive effect on metals themselves has been observed. Wegelin (*Zeit. Kolloid. Chem.* XIV. 65, 1914) has noted however that processes of mechanical disintegration of metals are greatly facilitated by the addition of gelatine. The metal particle which has adsorbed the gelatine is now less sensitive to precipitation by electrolytes and has in fact acquired properties more akin to an emulsion than to a suspension and is said to be "protected."

17. Protection of suspensions.

This decrease in sensitivity to electrolytes of a suspensoid by adsorption of a hydrated colloid from a solution provides a ready method for the estimation of the protecting power of these stabi-

lising colloids. The coagulation of gold sols is associated with a marked change in colour from red to violet and has been employed by Zsigmondy (*Zeit. f. Analyt. Chem.* XL. 697, 1901) as a standard for the estimation of protecting power which he expresses in terms of "gold numbers." The gold number of a protective colloid is that weight of colloid in milligrammes which will just permit the colour change in ten millilitres of a colloidal gold solution containing 0·0058 °/₀ of gold to occur on the addition of 1 m.l. of a ten per cent. sodium chloride solution.

The gold numbers of the various protective colloids vary greatly and indeed the method offers a means for the detection of substances otherwise not easily identified, e.g. the starches.

As typical of the gold numbers of various protective colloids the following values may be cited.

Albumen.		Starches.	
White of egg ...	0·08	Wheat starch	4—6
Albumin	0·1—0·3	Dextrin	6—12
Globulin	0·02—0·05	Potato starch	25
Ovomucoid ...	0·04—0·08		
Crystalline albumin	2—8		
Alkali albumin ...	0·0014—0·14		

Gum arabic	0·5
Gum tragacanth... ...	2
Gelatine	0·005—0·01
Isinglass	0·01—0·02
Casein	0·01
Na oleate...	0·4—1
Na stearate at 6° C. ...	10
" " 100° C. ...	0·001
Stannic acid	∞

Disintegration to the colloid state may also be bronght about by electrolytes. In general as has already been noted the ions of an electrolyte are not equally strongly adsorbed by a surface; owing to the preferential adsorption of one ion the surface acquires a charge of the same sign as the more strongly adsorbed ion, the cohesion between the particles is consequently lowered and although the interfacial surface tension is likewise reduced disintegration frequently results. The laws governing ionic adsorption will be

discussed in connection with coagulation by electrolytes. It may be noted in passing that relatively insoluble electrolytes which are those to which the method of disintegration with the aid of electrolytes is most readily applicable, adsorb their own ions most markedly and in consequence salts containing a common ion are most effective disintegrating agents. Thus hydroxides will disperse the hydrated oxides of zinc, aluminium and chromium; both silver and chlorine ions will disperse silver chloride. Sulphides may be disintegrated with the aid of hydrogen sulphide and many oxides by the formation of basic salts with chloride or nitrate ions.

The redispersion of a sol which has been precipitated by the addition of an electrolyte may also occasionally be effected by the removal of the precipitating agent through washing; thus certain precipitates such as silver chloride, zinc sulphide and copper ferrocyanide are readily redispersed in water where the precipitating salts are removed by thorough agitation and filtration.

18. Electrical dispersion methods.

Two methods of dispersion by electrical methods have been developed; one first investigated by Davy depends on the fact that where the current density at cathodes in suitable electrolytes exceeds a certain critical value the cathode undergoes disintegration. Davy noted the formation of a purple red suspension of tellurium by the cathodic disruption of a rod of the metal. Müller (*Zeit. Elektrochem.* XI. 521, 1905) confirmed this observation of Davy's and extended the method to selenium and sulphur by covering a platinum cathode with the fused elements. Metals such as lead, tin, bismuth, thallium, arsenic, antimony, and mercury are readily dispersed cathodically by electrolysis in alkaline solution at high current densities (Bredig and Haber, *Ber.* XXX. 2741, 1898; Haber and Saeck, *Zeit. Elektrochem.* VIII. 245, 1905, *Zeit. Anorg. Chem.* XXXIV. 286, 1903).

The mechanism of cathodic disintegration involves the formation of a metal alloy with a cation only deposited at high current densities and a large impressed electromotive force. Thus the disintegration of a lead cathode in alkaline solution is due to the formation of a lead sodium alloy which subsequently reacts with the water yielding a fine black dispersed lead suspension. This electrical dispersion

occurs still more readily in fused solutions as noted by Lorenz owing to the more effective disintegration effected by the fused electrolytes in comparison with water. Of more general utility is the arc dispersion method introduced by Faraday (*Proc. Roy. Inst.* 310, 1854) and developed by Bredig (*Zeit. Elektrochem.* IV. 514, 1899, *Zeit. Phys. Chem.* XXXI. 288, 1899). By forming an arc under various dispersion media such as water or organic liquids between wires formed of the metal, dispersion of the metal may be effected. A current of some ten amperes with a potential fall of some forty volts is usually sufficient to effect the dispersion of most metals such as platinum, gold, palladium, iridium and silver. Many metals in water give rise only to hydroxides when dispersed in this manner, e.g. aluminium, thallium, iron, copper and zinc, whilst the presence of small quantities of hydroxylions is desirable for producing fine dispersions of the more noble metals.

The thermal effects of the arc not only in promoting the oxidation of readily oxidisable dispersed metals but also in decomposing the dispersion media when organic liquids are employed was a serious objection to the method and attempts to improve the method which were finally successful were made by Svedberg (*Ber.* XXXVIII. 3616, 1905, XXXIX. 1705, 1906, *Methoden zur Herstellung Kolloider Lösungen*, 1909). By increasing the area of the electrodes and insertion of a condenser in parallel with the arc gap and reducing the current density of the arc Svedberg noted a great improvement in the purity of the metals dispersed in this way but decomposition of the medium was still marked when highly reactive metals such as the alkalis, or catalytic metals such as cobalt, nickel or platinum were employed, whilst several "hard" metals, e.g. aluminium, did not disperse readily when subjected to this treatment. By using an oscillating discharge from an induction coil as source of current and a condenser in parallel with the electrodes a great improvement in the purity of the dispersions or sols was achieved. By this method dispersions of various metals and metalloids in diverse media such as water, organic alcohols, ketones, ethers, chloroform and hydrocarbons have been prepared, the best results being obtained with short arcs in a system of low resistance, small inductance and large capacity.

The mechanism of colloid production by means of these immersed

arcs or sparks has not definitely been established. It has been noted that disintegration in the direct current arc occurs mainly at the cathode and it has indeed been suggested that these electrically produced dispersions are not the primary product of cathodic disruption but rather the result of an evaporation and secondary condensation and aggregation of metal vapour.

19. Methods of condensation.

The methods of disintegration rely entirely upon increasing the dispersity of a solid, which process can, at least theoretically, be stopped at any instant resulting in the formation of a suspension of definite dispersity but one that is not necessarily stable. The processes of suspension formation by methods of condensation on the other hand are more complicated, owing to the fact that unless the resulting colloidal suspension possesses at least some degree of stability the process of condensation once set in operation will not cease but proceed until the transformation to the macrocrystalline structure is complete.

The conditions of effecting condensation so as to produce a colloidal solution have been investigated in detail by von Weimarn (*Grundzüge der Dispersoidchemie*, 1911). The production of a colloidal solution by condensation according to von Weimarn is the result of two opposing forces in crystal formation, one, the interatomic forces of the material which tend to impart to the material its crystalline characteristics and the other the molecular kinetic processes comiug into play at the crystal surfaces; this factor is depeudent not only on the nature of the disperse material but also on the activity of the dispersion medium in relation to the disperse phase. Thus, according to von Weimarn, colloidal solutions whether dispersions, gelatinous precipitates or gels are in reality crystalline and built up of small crystals which under suitable conditions may link up one with another to form a network in which the dispersion medium may be retained. The conditions for forming colloidal solutions are thus dependent on the formation of small crystals which as has been pointed out are produced in solutions in which nucleus formation readily obtains, but where the subsequent growth of the minute nuclear crystals is relatively small.

The rate of nucleus formation is dependent both on the actual

amount of solute in the solvent and on its solubility, thus if a solution of sodium malonic ester in ligroin be added to a solution of chloracetic ester in the same solvent, by interaction an amount S of sodium chloride will be formed which by choice of suitable concentrations will exceed the actual solubility of sodium chloride in ligroin (s) by an amount $S-s$ or P. The rate of nucleus formation is in the first instance dependent on the velocity of initial condensation or the specific supersaturation

$$\frac{dn}{dt} = R\frac{S-s}{s} \text{ or } R\frac{P}{s} = U,$$

whilst the subsequent rate of growth of the nuclei once formed in the above manner is dependent as shown by Noyes and Whitney (see p. 191) on the diffusion coefficient as well as the absolute supersaturation of the solution x

$$\frac{dx}{dt} = \frac{D}{\delta}Sx.$$

These two equations thus define, according to von Weimarn, both the nature of the disperse phase produced by condensation and the life of the disperse in the form produced at the moment of separation.

The specific supersaturation U which determines the nature of the disperse phase must possess a large value for the rapid formation of many nuclei which is the condition for separation in the suspension or gel form. If the saturation concentration s be great a large amount of disperse phase will be produced for big values of U and we shall obtain a phase separation containing a great number of nuclei at small distances apart, i.e. conditions favourable to the formation of a bridged network or a gelatinous precipitate. If on the other hand the saturation concentration s be small the disperse phase separating for large values of U will be highly dispersed, conditions favourable for true dispersion or suspension formation.

With the guidance of the above considerations von Weimarn has been able to prepare a great number of inorganic salts in the colloidal form. As typical of a gradual transformation from the crystalline to the colloidal state of aggregation with increasing values of U, the following values for barium sulphate prepared by

the interaction of solutions of barium sulphocyanide and manganous sulphate may be cited.

Concentration of reagents in normality	$S-s$	$U=\frac{S-s}{s}$	Nature of precipitation
·00005–·00014	0–·0006	0–3	No precipitate in a year
·00014–·0017	·0006–·0096	3–48	Slow precipitation $U=8$. Momentary suspension stage at $U=25$. Complete separation in months to hours as large crystals
·0017–0·75	·0096–4·38	48–21,900	Precipitation in a few seconds at $U=48$. Beyond this instantaneous precipitations in crystal skeleton form. At $U=21{,}900$ crystals are barely recognisable
0·75–3	4·38–17·51	21,900–87,500	Immediate formation of "amorphous" precipitates
3–7	17·51–40·9	87,500–204,500	Clear cellular jelly

From these data it is evident that a momentary "suspension" stage is obtained for values of U equal to 8–25, but on attempting to increase the U values to obtain more definite persistence of the supension, a gel is formed; thus to prepare a colloidal suspension of barium sulphate a medium must be employed in which U values of 8–25 may be obtained at lower concentrations, i.e. we must reduce the actual solubility of barium sulphate. By performing the double decomposition in alcohol water mixtures in which the solubility of barium sulphate is small a clear stable suspension may in fact readily be formed.

The theory of von Weimarn thus accounts fully for both the appearance and stability of the colloidal phases in processes of condensation, but it is still an open question whether in fact the colloidal particles are entirely crystalline when prepared in this manner. The investigations of Scherrer (*Gött. Nachrichten, 1918*) with the Röntgen rays on colloidal gold and silver have indicated that they undoubtedly contain crystals, but it is more than probable that the individual particle does not consist of one crystal but rather consists of an aggregation of minute crystal elements held together by surface tension and possessing a marked surface energy; such a

composite particle could readily undergo transformation in size by aggregation or disintegration and could at the same time both by a process of solution and reprecipitation or by thermal agitation similar to the process of sintering be converted into the truly crystalline form possessing but little specific surface energy.

Methods of condensation in which protective colloids are employed, thus effecting condensation in the presence of a disintegrating agent, are largely employed for the preparation of stable suspensions, thus the precipitation of gold, platinum and palladium in the presence of gum arabic or the protalbic and lysalbic acids of Paal by means of reducing agents such as hydroxylamine, hydrazine, or formaldehyde readily results in the formation of remarkably stable suspensions.

CHAPTER VII

DIFFERENCES OF POTENTIAL AT INTERFACES

1. Origin of potential differences.

The electric potential throughout the body of a homogeneous phase is constant, but the possibility of obtaining an electromotive force from the terminals of a cell consisting entirely of homogeneous phases and their interfaces proves that in general there exist differences of electric potential across the latter.

Warburg (*Wied. Ann.* XLI. 1, 1890) observed that the surface tension of the interface between mercury and dilute acid decreases as the amount of the corresponding mercury salt present in the solution increases. He therefore concluded that the salt is positively adsorbed in accordance with Gibbs' adsorption equation. The adsorption by mercury of its salts from aqueous solution has been directly observed by McLewis (*Zeit. Phys. Chem.* LXXVII. 129, 1910), Patrick (*ibid.* LXXXVI. 545, 1914), Euler and Zimmerlund (*Arkiv Kemi, Min. Geol.* VIII. 14, 1921). Only the last mentioned attempted a quantitative estimation, but made no surface tension measurements by which Gibbs' equation might have been tested. McLewis was of the opinion that Gibbs' equation in the form $\Gamma = \frac{-d\sigma}{RTd\log c}$ would give the "pure" adsorption of undissociated molecules and that an additional term is required to cover the "electro-capillary" adsorption of each of the ions.

Warburg on the other hand used the theory of the concentration cell to relate the thermodynamic potential μ of the mercurous salt, measured in ergs per grm. equivalent with V, the excess of the electric potential of the mercury over that of the dilute acid containing the salt, expressed in volts thus:

$$d\mu = 96{\cdot}5 \times 10^{10}\, dV.$$

Hence Gibbs' adsorption equation takes the form

$$\Gamma = -\frac{d\sigma}{d\mu} = -\frac{d\sigma}{96{\cdot}5 \times 10^{10}\, dV}.$$

Schofield (*Phil. Mag.* March, 1926) has recently verified this relation by direct experiment. In order to appreciate the significance of this result, it is necessary to consider in more detail the electrical potential difference V and the manner in which it arises. Instead of regarding the phenomenon from the point of view of the Gibbs' equation, it has been, until recently, more usual to discuss the subject of electro-capillarity from the conceptions developed by Helmholtz and Lippmann. These views, together with the theory of electrolytic solution pressure advanced by Nernst, are not in reality incompatible with the principles of adsorption at interfaces as laid down by Gibbs.

2. The Helmholtz electric boundary layer.

Helmholtz (*Wied. Ann.* VII. 337, 1897) showed from electrostatic considerations that if M be the electric moment per sq. cm. of the interface expressed in electrostatic units then the difference of electric potential across the interface was related to the electric moment by the expression

$$V = 4\pi M \times 300. \qquad \text{.......................(1)}$$

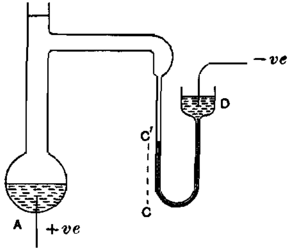
M the moment per sq. cm. in electrostatic units may be expressed more fully in terms of ρ, the volume density of charge at a distance x from an imaginary plane drawn somewhere in the non-homogeneous region between the phases, thus

$$M = \int \rho x \delta x. \qquad \text{..........................(2)}$$

In tbe bulk of each homogeneous phase ρ must be zero, hence the integral is finite. Moreover, like the moment of a couple its value is independent of the position of the plane about which it is taken.

Varley (*Phil. Trans.* A, CI. 129, 1871) first showed that a current could be caused to flow in a wire connecting two reservoirs of mercury immersed in an electrolyte when the mercury from one reservoir dropped through the electrolyte in the form of drops which coalesced in the other pool. He pointed out that this flow of mercury could be regarded as an expansion and contraction of the mercury snrface and that each drop as it falls carries down with it a positive charge from the upper to the lower electrode, thus completing the electrical circuit.

Lippmann (*Ann.* v. 494, 1875), independently made the same observation as a result of his study of the capillary electrometer.



This instrument consists essentially of a cell with a large mercury surface as anode and as cathode a mercury thread in a capillary tube CC'. As electrolyte, Lippmann used dilute sulphuric acid.

If the solution contains oxygen it reacts with the mercury on standing producing a small quantity of mercurous sulphate which renders the anode unpolarisable. We have already noted that the height DC' between the mercury in the reservoir and the capillary electrode surface is a measure of the interfacial surface tension. If an external E.M.F. be imposed upon the cell the mercury meniscus in the arm CC' will be observed first to fall to a minimum value and then to rise again with increasing applied E.M.F. On plotting the alteration of the interfacial surface tension against the applied E.M.F., Lippmann obtained a curve which within the limits of accuracy of his experiment was parabolic and rose to a well-defined maximum value.

Although there exists a concentration gradient of mercurous sulphate from the anode to the cathode it is unlikely that this causes an appreciable alteration in the electrical potential throughout the bulk of the electrolyte. Hence without serious error the applied E.M.F. V may be equated to the difference in the values of V at the two electrodes; and since V at the "unpolarisable" electrode remains unaltered the variation of σ with V is observed at the cathode. With the aid of thermo-dynamic reasoning, Lippmann deduced the relation

$$\frac{d\sigma}{dV} = -\epsilon \times 10^7, \quad \text{.......................(3)}$$

where V is measured from the electrolyte to the metal and ϵ is the charge per unit area of mercury surface, or more precisely the charge which must be given to a mercury electrode when its area *increases by unity in order to maintain the potential difference* between it and the electrolyte unaltered.

3. Helmholtz's theory of the electric double-layer.

Helmholtz pointed out that an interface would have an electric moment if it contained two planes carrying an equal and opposite surface density of charge separated by a small distance. He called this imaginary arrangement an electric double-layer. Although of the opinion that in general the moment of an interface cannot be regarded as due to so simple a distribution of electricity, he put forward the view that such a distribution actually exists at a polarised electrode, the double-layer being made up of a charge on the metal and an equivalent number of ions of opposite sign a short distance away.

In 1881, Helmholtz took the further step of identifying ϵ of Lippmann's equation with the charge on the metal side of the double-layer (*Monats. König. Preus. Akad. Wiss. Berlin*, 1881, p. 947). From this assumption two deductions follow at once.

(1) that at an electrolyte-mercury interface showing its maximum surface-tension $V=0$ since $\epsilon=0$ by Lippmann's equation,

(2) that since by (1) $V=V_{\text{max.}}-V_1$ the thickness δ of the double-layer is given by

$$\delta=\frac{M}{\epsilon}=\frac{V}{4\pi\epsilon}. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

If we consider the electric boundary layer to consist of orientated molecules of constant moment perpendicular to the surface, this would give a constant value of δ and a parabolic electro-capillary curve. Hence the outward force the molecules exert will be inversely proportional to the square of the area they occupy and thus *inversely proportional to the fourth power of their distance apart* *, a result in agreement with the known properties of doublets.

The σ, V, or electro-capillary, curve for dilute sulphuric acid of a strength used by Lippmann is almost exactly parabolic and

* From Lippmann's equation $d\sigma=\epsilon dV$, if δ be constant $V=K\epsilon$ or $d\sigma=K\epsilon d\epsilon$ or $F=\sigma-\sigma_0=K'\epsilon^2=K'\Gamma^2=\frac{K'}{A^2}=\frac{K'}{r^4}$.

hence gives a nearly constant value of δ. Lippmann therefore believed the double-layer to have a thickness independent of the sign and magnitude of ϵ. This electrolyte is, however, peculiar and Gouy (*Ann. de Phys.* VI. 5, 1916; VII. 29, 149, 1903) showed that in general $V_{max.} - V_1/4\pi\epsilon$ is not constant as will be seen from the following table:

$V_{max.} - V_1$ in volts	δ from the expression $\delta = \frac{V_{max} - V_1}{4\pi\epsilon}$ in Å, in the following electrolytes			
	H_2SO_4 (16°/o)	$KNO_3\,M$	$Na_2SO_4\,\frac{M}{20}$	$KI\,\frac{M}{10}$
+1·0	·241	—	—	—
+ ·8	·321	—	—	—
+ ·6	·338	·312	·232	—
+ ·4	·324	·302	·236	·058
+ ·2	·295	·260	·264	·120
− ·2	·278	·310	·372	·201
− ·4	·339	·375	·413	·273
− ·6	—	·410	·445	·338
− ·8	—	·472	·468	·376
−1·0	—	—	·479	·384
−1·2	—	—	·483	—
−1·4	—	—	·475	—

At the beginning of the present century, when molecular magnitudes became more exactly known, it became apparent that δ was smaller than an atomic diameter. It was therefore suggested that the charges of the double-layer must be regarded as separated by a dielectric medium*. The thickness of the double-layer is increased eighty-fold if pure water be regarded as the intervening medium, but even if the dielectric constant of so thin a layer be considerably less than that of water in bulk the thickness will still be of a possible order of magnitude. The variations in δ may thus be attributed to a variation either in the thickness of the douhle-layer or in the effective dielectric constant, or to a combination of both causes.

* Equations (1) and (2) contain no reference to a dielectric constant because in evaluation of *M all* the charges are considered. These in the system under discussion would include the charges induced in the dielectric medium as well as those of the metal surface and its complementary layer of ions.

4. The variation of V at the maximum of the electro-capillary curve.

If V is zero at the maximum of the electro-capillary curve, it is evidently possible to find the absolute potential difference at a standard electrode by using it as the anode of a capillary electrometer and observing the E.M.F. which must be applied to reach the maximum of the electro-capillary curve. As a result of numerous experiments, Gouy (*Ann. de Phys.* VI. 5, 1916) concluded that the necessary E.M.F. varies with the electrolyte used at the capillary. It was thought that this might be due to liquid-liquid potential differences at the junctions between these electrolytes and that of the standard electrode. Nernst investigated the theory of these potential differences and showed them to be due to the diffusion of salts whose ionic mobilities differ. Smith (*Phil. Trans.* A, CXCIII. 70, 1900) therefore performed an experiment, which involved only a junction, KCl and KI solutions of the same strength between which the diffusion potential difference is negligible. He proved that if Nernst's theory is correct V cannot in all cases be zero at the maximum of the electro-capillary curve, since using a decinormal calomel electrode as anode the maximum occurs at an applied E.M.F. of 0·56 or 0·79 volt according as $N/10$ KCl or $N/10$ KI is used at the capillary.

Nevertheless, for many electrolytes the maximum is attained for an applied E.M.F. which differs very little from 0·53 for the decinormal calomel or 0·48 for the normal calomel electrode, and it has been several times suggested that the simple Helmholtz theory is applicable in such cases, but that for electrolytes such as KI which are in some way "abnormal" it requires modification. Krüger (*Gesell. Wiss. Göttingen Nachr. Math.-Phys.* (1), XXXIII. April 30, 1904), after critically discussing the views of previous writers propounded the view that "abnormal" electrolytes which give "displaced" maxima form complex ions with mercury and hence Lippmann's equation requires modification when such electrolytes are used. Gouy showed, however, that many organic compounds dissolved in the electrolyte displace the maximum; Krüger's theory is evidently inapplicable here. Later (*Zeit. Elektrochemie*, XIX. 617, 1913), Krüger and Klemensiewicz attempted to show that the capillary curve for normal KNO_3 is accurately parabolic and argued that for this solution alone $V=0$ at the maximum. The δ-values

for KNO_3 given in the table, however, show that the curve is not an exact parabola, and although their variation from a mean value is less than those for some other solutions the choice is quite arbitrary.

5. Experimental verification of Lippmann's equation.

Lippmann's method of deducing equation (3) has been criticised on the ground that it ignores the "residual" current which continues to traverse a capillary electrometer after the surface charge on the cathode has taken up the value corresponding to the E.M.F. applied. Gouy upholds Lippmann's treatment contending that this is an irreversible effect which may be disregarded in a thermodynamic treatment.

The dropping electrode used by Paschen and improved by Palmaer must when insulated take up such a potential that $\epsilon = 0$ since the drops cannot carry away a charge without altering its potential. For some time it was uncertain whether the potential of the dropping electrode always corresponds exactly to that of the maximum surface tension, as it must be if Lippmann's eqnation is always valid. The very careful experiments of Smith and Moss (*Phil. Mag.* VI. XVII. 833, 1909) and more recent measurements of Frumkin (*Zeit. Phys. Chem.* CIII. 56, 1922) show clearly that this is the case for electrolytes which give "displaced" as well as "normal" maxima and also in the presence of organic substances. Frumkin has also made quantitative observations on apparatus similar in all essentials to that of Varley and Lippmann (p. 209). By determining the size and number of the drops which cause the passage of the charge measured by the galvanometer he obtained an experimental measure of the charge carried down per unit area of drop surface. In the following table the directly observed values of ϵ are compared with the corresponding values of $d\sigma/dV$. The

Solution	ϵ microcoulombs/cm.^{2}	$d\sigma/dV$ microcoulombs/cm.^{2}
n-NaCl with Hg_2Cl_2	47	50
n-KOH with HgO	17	21
$2n$-H_2SO_4 with Hg_2SO_4	39	39
n-KNO_3 + ·01n-KI with KI . HgI_2 ...	90	86
n-KOH + $(C_2H_5)_2O$ with HgO ...	−1·3	−1·5

results are in complete accord with Lippmann's equation and further prove that it is valid entirely irrespective of the composition of the electrolyte.

Lippmann's equation is thus shown to be completely valid in spite of the shortcomings of the simple double-layer theory.

On page 208, we noted that Gibbs' adsorption equation takes the form

$$\Gamma = - \frac{d\sigma}{96{\cdot}5 \times 10^{10}\, dV}.$$

This, combined with Lippmann's equation, which we have seen has received experimental confirmation in many ways, leads to the result

$$\epsilon = 96{\cdot}5 \times 10^{8}\, \Gamma.$$

Lippmann's equation may thus be regarded as identical with that of Gibbs expressed in the form given to it by Warburg.

Since both the metal and the electrolyte with which it is in contact are conductors and since there can be no net charge in the *interior of a conductor, imparting a charge to the electrode must* involve the flux of the same quantity of electricity *across* the interface. This electric flux may be regarded as producing at the interface the necessary surface concentration of mercurous salt. The essential connection between the adsorption of mercurous salt and the charge per unit area has been traced by Schofield*, by using Nernst's theory of electrode potential in a generalised form, which does not involve the physical existence of an electrolytic electrode solution pressure or the erroneous idea current when Nernst developed his theory that a metal is always at the same electrical potential as an electrolyte with which it is in contact when it carries no surface charge.

6. Application of Gibbs' equation to ionic adsorption.

According to Gibbs, any constituent of a system in equilibrium must have the same thermo-dynamic potential in all the phases of which it is a component. Hence, when eqnilibrium has been established across an interface between a metal and an electrolyte containing its ions, the thermo-dynamic potential $\mu_{Me\ \text{ions}}$ of the metallic ions must be the same in both. In general the thermodynamic potential of a constituent which is electrically neutral may be said to depend only on its concentration C and its "environment," but if it is an ion the electrical potential of the phase

* *Phil. Mag.* I. 641, 1926.

must also be considered. In the present system if the electrical potential of the electrolyte be reckoned as zero and that of the metal V (in volts) the thermo-dynamic potential of the metallic ions in ergs per grm. ion will be

$$\left.\begin{aligned}\mu_{Me\,\text{ions}} &= RT\log_e c + k_e \text{ for the electrolyte} \\ &= 96{\cdot}5 \times 10^{10} nV + k_m \text{ for the metal}\end{aligned}\right\} \quad \text{.........(1)}$$

where k_e represents the "environment" in the electrolyte and is only independent of c when the latter is small, $96{\cdot}5 \times 10^{10} n$ is the charge on a grm. ion in coulombs $\times 10^{-7}$, n is the valency of the metallic ions, and k_m embraces both the concentration and "environment" in the metal and is evidently independent of c. Hence,

$$V = (RT\log_e c - \{k_m - k_e\})/96{\cdot}5 \times 10^{10} n.$$

In this relation $k_m - k_e$ is proportional to the logarithm of Nernst's "ionic solution pressure," but is seen to depend on the properties of the electrolyte as well as on those of the metal*.

Were it supposed that at an interface the density of each component changed abruptly at an imaginary geometrical surface, being constant on either side into the interior of each phase, the amount of each component actually present in the system would differ from that calculated on this hasis by an amount depending on the position chosen for this dividing surface. By a suitable choice, however, the surface excess of any one component can be made to vanish, and in the present system it is convenient to so choose it, that there is no surface excess or deficit of metallic ions at the interface, since these are the one constituent present in both phases. In accordance with this convention all the metallic ions in the system are assigned to one or other of the bulk phases.

If when a metal comes into contact with an electrolyte, e.g. mercury in contact with dilute sulphuric acid containing mercurous sulphate it is not at the electrical potential necessary for equilibrium; the thermodynamic potential of the metallic ions in the two phases will differ and consequently some of them will pass across the boundary or compensating adjustment of the surface will take place.

* Butler, *Trans. Faraday Soc.* XIX. 729, 1924, and Heyrovsky, *Roy. Soc. Proc.* A, CII. 627, 1923, have given expressions relating V to the molecular properties of the metal and the electrolytes. Their treatments may be regarded as attempts to evaluate k_m and k_e in terms of the ionisation potential of the metal and the heat of hydration of the ions in the solvent respectively.

This passage of ions may be conveniently called the Nernst ionic transfer.

We have seen, however, that according to Helmholtz the potential difference between the two phases is given by

$$V = 4\pi M . 300.$$

Hence, two phases in contact can only be at a difference of electric potential V when the electrical distribution in the interfacial layer gives rise to the necessary moment. Thus, although the equilibrium value of V is determined solely by the chemical composition of the two homogeneous phases, a particular molecular and ionic arrangement must be established in the intervening non-homogeneous layer in order that the conditions of chemical and electrical equilibrium may be simultaneously obeyed.

The Nernst ionic transfer of ions to the metallic phase will give rise to a surface deficiency of electrons (the other component of the phase), similarly their removal will cause a surface excess of electrons. Since there can be no net volume charge the surface density of the other ions of the electrolyte with respect to the dividing surface must always have a charge equal or opposite to that of the surface density of electrons. The resulting distribution will give rise to an electric moment the value of which for a bulk phase of given composition will depend only on the surface density of electrons. The exact relation between these two quantities cannot be deduced from general principles unaided by specific molecular hypotheses. In spite of this it is evident that the "Nernst ionic transfer" will continue until the resulting surface density of electrons is sufficient to set up the moment necessary to give the value of V required for the equilibrium of the metallic ions.

In the system under consideration the independently variable components are the ions $Hg_2^{\cdot\cdot}$, SO_4'', $H^{\cdot}$, OH' and electrons, since all the constituents present can be regarded as composed of two or more of these.

If a change of σ with V be considered in which the strength of the sulphuric acid remains constant $d\mu$ for SO_4'', $H^{\cdot}$ and OH' is zero. $d\mu_{Hg_2^{\cdot\cdot}}$ is likewise zero on account of the choice of the dividing surface. Thus on application of the Gibbs' equation

$$d\sigma = -\Sigma\, \Gamma d\mu$$

in which the summation extends over all the independent variable

components of the system, we obtain only the term relating to the electrons remaining or

$$\Gamma_{\text{electrons}} = -\frac{d\sigma}{d\mu_{\text{electrons}}} = -\frac{d\sigma}{96{\cdot}5 \times 10^{10} dV},$$

$\Gamma_{\text{electrons}}$ being measured in grm. equivalents per sq. cm. If $\Gamma_{\text{electrons}}$ be replaced by its equivalent in coulombs per. sq. cm. we obtain Lippmann's equation

$$10^7 \times \epsilon = -\frac{d\sigma}{dV}.$$

It thus appears that the surface concentration calculated with the aid of Gibbs' equation is equal on the one hand to minus the surface charge found by Lippmann's equation from the slope of the electro-capillary curve and on the other hand to minus the number of grm. equivalents of mercurous ions taken up by an expanding mercury surface or thrown off a contracting one in the course of the Nernst ionic transfer.

Whether the diminution in mercurous salt concentration of a solution in contact with an expanding mercury surface be regarded as due to the adsorption of the salt on the newly formed surface as imagined by Gibbs and Warburg or as due to the transference of mercurous ions from the aqueous to the metallic phase as postulated by Lippmann and Nernst, we have seen that the number of grm. equivalents removed from the solution per unit increase in area is equal to $\frac{1}{96{\cdot}5 \times 10^{10}}$ of the slope of the corresponding electro-capillary curve. Schofield found it easier in practice to test this relation by finding the increase in concentration of a solution flowing steadily over a mercury surface into which drops having previously come to equilibrium with the solution coalesced. The drops were counted by means of a rotating disc with radial slits mounted on a Rayleigh Wilberforce synchronous motor. By finding the weight of a given number of drops the area of each drop and hence the area removed per second was calculated. The number of grm. ions thereby thrown off into the solution as it flowed past was found by adjusting a current which, flowing between a still mercury surface as anode and a platinum foil in a side tube, caused an alteration in the mercurous ion concentration to yield the same increase in E.M.F. Potentiometer observations were made to

detect changes in mercurous ion concentration. The following table *shows the agreement between the observed adsorption and that calculated* from the slope of the corresponding electro-capillary curve.

E.M.F. (function of $C_{Hg^{\cdot\cdot}}$) millivolts	Γ directly measured grm. equivalents/cm.$^2 \times 10^{10}$	Γ calculated from slope of capillary curve, i.e. by Gibbs' equation grm. equivalents/cm.$^2 \times 10^{10}$
18·0	4·23	4·10
30·5	3·69	3·55
42·0	3·10	3·20

7. The structure of the boundary layer.

Neither Gibbs' equation nor that of Lippmann gives us any information as to the structure of the boundary layer. Helmholtz, as we saw, considered it to consist of a charge on the metal surface separated from a layer of ions of opposite sign situated at a small distance from the surface. He did not, however, enquire how these ions were kept separate from the surface or whether the charges should be considered as separated by a dielectric medium.

From Helmholtz's equation it is possible to calculate the equivalent thickness of the double layer, δ, as well as the electric moment M, i.e. the distance to which a proton and an electron must be separated, in vacuo, to give the same electric moment. From a knowledge of V and Γ we are in a position to calculate the electric moment of each adsorbed molecule, a few of these are given in the following table:

Substance	Interface	Electric moment per molecule in Å.U. for	
		$\Gamma = 1 \times 10^{-10}$ grm. mols. per sq. cm.	$\Gamma = 2 \times 10^{-10}$ grm. mols. per sq. cm.
n-Butyric acid ...	Water-air	0·06	0·06
Tertiary amyl alcohol	Water-mercury	0·05	0·05
Cane sugar	"	very small	very small
Potassium iodide ...	"	0·24	[0·15]
Mercurous sulphate	Dilute acid-mercury	0·23	0·20
Sodium oleate ...	Borate buffer—oleic acid	[0·2]	[0·15]

Whilst the electric moment so calculated is in reality not an absolute value since it is actually only the alteration in electric moment of the surface produced by substituting the adsorbed solute molecules for solvent molecules, yet it is clear that the ionisable substances possess large values which vary within wide limits as the surface concentration is altered. We must conclude that since the apparent molecular electric moment varies with the concentration that Helmholtz's conception of a rigid double layer must be replaced by some species of boundary layer which varies in structure with the surface concentration. Gouy (*loc. cit.*) was the first to consider in detail the mechanism by which the ions are kept away from the charged surface. He put forward the view that the finite value of δ is due to their thermal agitation. On this idea the solution say of $\frac{M}{10}$ NaCl is of uniform concentration at some distance from the electrode but if it is charged negatively the concentration of the cations increases as its surface is approached and that of the anions decreases; the osmotic forces which tend to re-establish a uniform concentration being balanced at each point by the electric force due to the potential gradient. On the assumption that the ions were point charges in ideal solution of dielectric constant 80, Gouy calculated the distance of the "centre of gravity" of the volume charge caused by the excess of cations and deficit of anions from the electrode surface as a function of the concentration of the solution and the surface charge ϵ. The following are the values calculated for a decinormal solution of a uni-univalent salt together with the observed values for sodium chloride.

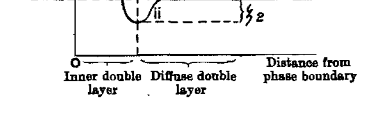
ϵ	Distance of c.g. in cms. $\times 10^{-8}$	δ in cms. $\times 10^{-11}$	δ observed cms. $\times 10^{-11}$
0·0	9·6	100	
0·0019	9·6	120	
0·017	9·1	114	350
0·33	7·5	94	to
0·89	5·4	68	490
1·84	3·5	44	
2·60	3·1	39	

The discrepancy between observed and calculated values is considerable. Furthermore, on Gouy's theory of a "diffuse" boundary

layer δ should vary inversely as the square root of the concentration, actually it varies very little either with ϵ or the concentration.

These considerations lead us to the conclusion that the structure of the boundary layer is neither of the parallel unimolecular sheet type suggested by Helmholtz nor diffuse as postulated by Gouy. Since the ions close to the surface do not actually fall into the surface it is clear that part of the boundary layer must be regarded as sheet-like in character whilst the following simple calculation shows that part must also be diffuse. At a negatively charged surface in $\frac{M}{10}$ NaCl the anions are in deficit to the extent of $0{\cdot}15 \times 10^{-10}$ grm. ions per sq. cm. The solution contains 10^{-4} grm. ions per c.c., hence the slice thickness which must be denuded is $1{\cdot}5 \times 10^{-7}$ cms., since the tailing off is gradual in character this thickness is a minimum estimate of the thickness of the diffuse layer.

The boundary layer structure is thus complex consisting in general of two parts, an inner condenser-like double layer and an outer or diffuse layer. It is probable that the sheets of the inner layer are separated by but one layer of water molecules possessing a dielectric constant of about 7, the diffuse layer stretching a not inconsiderable distance into the aqueous phase. It is clear that the potential gradient giving rise to V the interface potential is not uniform but is probably steeper over the inner double layer and falling off more gently across the outer or diffuse layer. In some cases at least it is possible that a *twofold ionic stratification* may exist before the outer layer is reached, the potential distance curve thus presenting a point of inflexion as indicated by (ii) in the following diagram.



In addition to the interphase potential difference V there exists another potential difference of fundamental importance in the theory of the electrical properties of colloids namely the electrokinetic potential, ζ, of Freundlich. As we shall note in subsequent sections the electrokinetic potential is a calculated value based upon certain assumptions for the potential difference between the aqueous bulk phase and some apparently immobile part of the boundary layer at the interface. Thus ζ represents a part of V but there is no method yet available for determining how far we must penetrate into the boundary layer before the potential has risen to the value of the electrokinetic potential ζ, whether in fact ζ represents part of, all or more than the diffuse boundary layer. It is clear from the above diagram that ζ bears no relation to V, the former may be in fact either of the same or opposite sign, a conclusion experimentally verified by Freundlich and Rona.

8. Motion due to the electrokinetic potential.

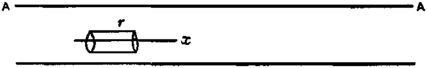
If charcoal be immersed in dilute hydrochloric acid the hydrogen ons are adsorbed more readily than the chlorine ions. Owing however to the electrostatic attraction between the ions of opposite sign, a diminution in the equilibrium surface concentration of the hydrogen ions, and an increase in excess of the equilibrium concentration of the chlorine ions occurs. The system as a whole is electrically neutral, but between the charcoal and the solution a difference of potential will be created, a measure of the excess of hydrogen ions over chlorine ions adsorbed. The solid will thus acquire a charge relative to the liquid, and on impressing an E.M.F. on the system, the liquid will move past the solid, if this be kept stationary, a phenomenon termed electric endosmose; whilst if the solid be present as small particles these will move through the solution to one or other of the electrodes, a motion to which the term electric cataphoresis has been applied.

9. Electric endosmose.

In 1808 Reuss (*Mém. de la Soc. de Moscou*, II. 327, 1809) observed that on passage of an electric current through a cell containing an earthenware diaphragm the electrolyte was transferred from the anode to the cathode compartment. Porret (*Pogg. Ann.* LXVI. 272,

1816, 618, 1828) observed a similar phenomenon with a sand diaphragm. Wiedemann (*Pogg. Ann.* LXXXVII. 321, 1852, XCIX. 177, 1856) was, however, the first to conduct a series of systematic experiments on the subject. The theory that any electric "double layer" was the cause of the phenomenon was first suggested by Quincke (*Pogg. Ann.* CXIII. 513, 1861) and developed by Helmholtz (*Ann. de Phys. Chim.* VII. 337, 1879, *Ges. Abhandlungen*, I. 855, 1882).

The *relationship between the quantity of liquid transported* and the current has been developed in the following manner by Porter (*Trans. Farad. Soc.* XLVIII. 133, 1921).



Consider the stream line flow of liquid through a narrow capillary tube AA of cross-sectional area A to which a longitudinal voltage $V_1 - V_2$ is applied so as to be uniform across the cross-section. If there is a charge q anywhere in the liquid the force acting on the charge is $-q\frac{dV}{dx}$.

We select a cylinder of unit length and radius r enclosing the charge q, then the total normal induction over the cylinder is, by Gauss's theorem, $\frac{4\pi q}{K}$ where K is the specific inductive capacity of the liquid. The curved area of the cylinder is $2\pi r$ and the electric force outwards from the curved surface is

$$-\frac{dV}{dr},$$

hence
$$\frac{4\pi q}{K} = 2\pi r\left(-\frac{dV}{dr}\right).$$

When a steady flow u is set up the longitudinal force on the charge balances the frictional force against the curved area or

$$-q\frac{dV}{dx} = -2\pi r\eta\frac{du}{dr},$$

where η is the viscosity.

Eliminating q we obtain

$$K\frac{dV}{dr}=\frac{4\pi\eta\frac{du}{dr}}{-\frac{dV}{dx}}.$$

The electric current C is by Ohm's law equal to

$$-\frac{dV}{dx}\frac{A}{R},$$

where R is the specific resistance of the liquid.

Hence $$\frac{dV}{dr}=\frac{4\pi\eta A}{KRC}\frac{du}{dr}.$$

This equation is independent of the particular distribution of the electric charge across the cross-section.

If V_m and u_m are the potential and velocity at a point on the tube axis and V_w and zero the corresponding values for the tube wall

$$V_m-V_w=\zeta=\frac{4\pi\eta A}{KCR}u_m.$$

If the charges in the liquid forming part of the double layer are in close proximity to the tube wall there will be no charge in the bulk of the liquid, i.e. $q=0$ or $\frac{du}{dr}=0$, thus the liquid will move through the tube with a uniform velocity equal to u_m.

The total liquid flow will consequently be $u_mA=U$ say. Hence

$$U=\frac{KRC}{4\pi\eta}(V-V_w)=\frac{KRC}{4\pi\eta}.\zeta$$

where ζ is the transverse voltage or electrokinetic potential

$$=\frac{KA}{4\pi\eta}\times\text{longitudinal voltage}\times\text{transverse voltage}.$$

The transverse voltage ζ is the drop of potential across the double layer and is of the order of 0·01 to 0·05 volt. It will be noted that the amount of liquid transported is dependent on the nature of the liquid and on the current and is independent of the diameters or lengths of the tubes of the diaphragm. Somewhat divergent views are held as to the actual thickness of the double layer (Lamb, *Phil. Mag.* xxv. 52, 1888) a point which we have already referred to.

In a similar manner the actual hydrostatic pressure difference P produced by electric endosmose can be calculated, with the following result:

$$P = \frac{2\zeta(V_1 - V_2)K}{A}.$$

On forcing a liquid through a diaphragm, diaphragm currents are set up, a phenomenon noted by Wiedemann and Quincke and one fully accounted for on the hypothesis of the existence of an electrical double layer between the diaphragm material and the liquid.

As has been indicated above the formation of the electric double layer of potential ζ is attributed to the selective or preferential adsorption of one ion. The influence of the nature of the electrolyte on both the magnitude and sign of the electric double layer as indicated by electric endosmose experiments was first studied in detail by Perrin (*Journ. Chim. Phys.* II. 601, 1904, III. 50, 1905; see also Hittorf, *Zeit. Phys. Chem.* XXXIX. 613, 1902, XLIII. 239, 1903; Baudouin, *C.R.* CXXXVIII. 898, 1904; Ascoli, *C.R.* CXXXVII. 1253, 1903; Guillaume, *C.R.* CXLVII. 53, 1908; Elissafoff, *Zeit. Phys. Chem.* LXXIX. 385, 1912; Bethe and Toropoff, *Zeit. Phys. Chem.* LXXXVIII. 686, 1914, LXXXIX. 597, 1915; Glixelli, *Bull. de l'Acad. des Sciences de Cracovie,* A, 102, 1917; Gyemant, *Koll. Zeit.* XXVIII. 103, 1921). The general conclusions in regard to the influence of various electrolytes on electric endosmose may be briefly summarised as follows:

In accordance with theoretical expectations only strongly ionising solvents exhibit marked endosmose, e.g. chloroform and benzene are practically inert whilst nitrobenzene, the alcohols and water exhibit the phenomenon to a marked extent. Of the ions adsorbed by materials constituting the diaphragms, as in the case of direct adsorption, the hydrogen and hydroxyl ions have the greatest influence. In acid solutions most diaphragm materials acquire a positive charge relative to the liquid which moves to the anode, in alkaline solutions hydroxyl ions are adsorbed and the liquid moves to the cathode being positive relative to the negatively charged diaphragm.

If the solid diaphragm material adsorbs both hydrogen and hydroxyl ions it is evident that electric endosmose will cease when equal ionic adsorption has taken place, the double layer potential or electrokinetic potential being at this point zero and the diaphragm is at the isoelectric point.

No substance examined appears to have an isoelectric point identical with pure water $P_H = 7$ where the solution contains identical concentrations of both hydrogen and hydroxyl ions and in general *most materials adsorb hydrogen ions more readily than hydroxyl ions.*

In the following tables are given the concentrations of solutions necessary to change the sign of a few typical diaphragms and the relative rates of electric endosmose through diaphragms of identical thickness.

Diaphragm material	Solution	Diaphragm charge	Relative rate of electric endosmose
AgCl	$\frac{N}{500}$ HCl	+	3
	$\frac{N}{500}$ NaOH	−	5
$CrCl_3$	$\frac{N}{1000}$ HCl	+	9·5
	$\frac{N}{500}$ KOH	−	8·5
Blood charcoal ...	$\frac{N}{100}$ HCl	+	2·6
	$\frac{N}{1000}$ HCl	+	1·4
	$\frac{N}{20,000}$ HCl	+	0·7
	$\frac{N}{50,000}$ HCl	−	0·4
Gelatine	$\frac{N}{50}$ HCl	+	2·2
	$\frac{N}{100}$ NaOH	−	3·5
Kaolin	$\frac{N}{10}$ HCl	0	0
	$\frac{N}{100}$ HCl	−	0·6
	$\frac{N}{1000}$ HCl	−	6·1
	$\frac{N}{1000}$ NaOH	−	18·2

Agar-agar, collodion and cellulose appear always negative except in strongly acid solutions. Various relatively insoluble bases and acids have been employed as diaghragm materials by Glixelli (*Bull. de l'Acad. des Sc. Cracovie*, 1917) and Gyemant (*Koll. Zeit.* XXVIII. 103, 1921), and as anticipated the isoelectric points of the basic

diaphragms are found in weakly alkaline solutions, of the acid diaphragms in acid solution, as indicated by the following data:

	Solution	Diaphragm charge	Relative rate of endosmose
Basic diaphragms:			
Fe_2O_3	H_2O	+	10·50
	0·001*N* HCl	+	67·00
	0·0001*N* $AlCl_3$	+	103·00
	0·001*N* NaOH	−	16·00
ZnO	H_2O	+	0·31
	·0002*N* NaOH	+	0·22
	·0003*N* NaOH	−	0·16
	·0004*N* NaOH	−	0·24
$Mg(OH)_2$	H_2O	+	0·64
	·0006*N* NaOH	+	0·05
	·02*N* NaOH	−	0·90
Acid diaphragms:			
Silica	H_2O	−	0·63
	0·03*N* HNO_3	−	0·33
	0·47*N* HNO_3	−	0·12
Tungstic acid ...	H_2O	−	2·66
	0·045*N* HCl	−	1·12
	0·207*N* HCl	−	0·28
	0·8*N* HCl	−	0·00

In the case of adsorption on charcoal it is found that the organic ions are more strongly adsorbed than either hydrogen or hydroxyl. Whilst the other cations and anions are adsorbed to varying extents, the position of the ion in the electropositive series, the mobility and the valency appear to be the dominating influences.

Freundlich (p. 355) gives the following values calculated from endosmotic rate experiments for the concentrations of various electrolytes necessary to produce an identical diminution in the double layer potential or ζ values.

Electrolyte	Concentration in millimols. per litre	
	Oil-water interfacial potential reduced from 0·046 to 0·037 volt	Glass-water interfacial potential reduced from 0·089 to 0·039 volt
KCl ...	24	25
$BaCl_2$ ...	0·450	0·870
$AlCl_3$ ...	0·010	0·020
$ThCl_4$ ...	0·005	0·015

In the case of acids the hydrogen ion is more strongly adsorbed than the anion giving the diaphragm a positive charge. If however the acid containing a feebly adsorbed anion, e.g. chloride ion, be replaced by one containing a more strongly adsorbable anion, e.g. SO_4'', the double layer potential due to the difference in electrostatic charge will be diminished and the velocity of electric endosmose reduced as is shown by the following data obtained by Perrin (*loc. cit.*):

Diaphragm	Solution	Diaphragm charge	Relative rate of electric endosmose
Al_2O_3	$\frac{N}{1000}$ HNO_3	+	10·0
	$\frac{N}{1000}$ HCl	+	10·0
	$\frac{N}{1000}$ H_2SO_4	+	1·5

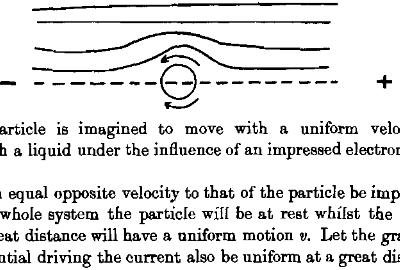
In some cases with a strongly adsorbed anion actual reversal of sign may take place, e.g.

Diaphragm	Solution	Diaphragm charge	Relative rate of electric endosmose
$CrCl_3$	Dilute acid	+	5·9
	$+\frac{N}{1000}$ $K_3Fe(CN)_6$	+	0·2
	$+\frac{N}{50}$ $K_3Fe(CN)_6$	−	2·0
Mn_2O_3	Dilute alkali	−	4·0
	$+\frac{N}{500}$ $Ba(NO_3)_2$	+	1·8
	$\frac{N}{50}$ HCl	+	3·8
Naphthalene ...	$\frac{N}{100}$ HCl	+	3·9
	$\frac{N}{1000}$ HCl	+	2·8
	$\frac{N}{5000}$ HCl	+	0·3
	$\frac{N}{5000}$ KOH	−	2·9
	$\frac{N}{1000}$ KOH	−	6·0
	$\frac{N}{50}$ KOH	−	6·0

The attainment of a definite maximum for this transverse potential can readily be demonstrated in that a maximum rate of endosmotic flow is obtained on the addition of electrolyte in increasing concentrations, a phenomenon well marked in the case of naphthalene.

10. Electric cataphoresis.

Preliminary data on cataphoresis or the rate of migration of a charged particle through a solution under the influence of an applied potential difference were made by Quincke (*loc. cit.*) and Linder and Picton (*J.C.S.* LXI. 67, 1887), whilst accurate measurements have been made by Burton (*Phil. Mag.* 6, XI. 440, 1906, XII. 474, 1906), Ellis (*Zeit. Phys. Chem.* LXXVIII. 321, 1912), Powis (*ibid.* LXXXIX. 91, 1915), Svedberg (*Koll. Zeit.* XXIV. 156, 1919), Cotton and Mouton (*Les Ultramicroscopes*, ch. 7). The following development is given by Porter (*loc. cit.*), for the influence of the double layer potential ζ and the physical constants on the velocity of migration.



A particle is imagined to move with a uniform velocity v through a liquid under the influence of an impressed electromotive force.

If an equal opposite velocity to that of the particle be impressed on the whole system the particle will be at rest whilst the liquid at a great distance will have a uniform motion v. Let the gradient of potential driving the current also be uniform at a great distance and equal to G both v and G being parallel to x.

At a great distance the potential will be given by $V = -Gx$, whereas near the particle additional terms will enter, due to the disturbance introduced by the presence of the particle. When the motion is slow it is irrotational and can be derived from differentiating a potential function ϕ; at a great distance $\phi = -Vx$.

Assuming a slip (Lamb, *loc. cit.*) at the surface of the particle $u_0 = -\frac{d\phi}{dS}$; the corresponding force due to friction on unit area is $-\beta\frac{d\phi}{dS}$, where β is the coefficient of friction.

The force on the charge of the element is $-q\frac{dV}{dS}$ and for steady motion

$$\beta\frac{d\phi}{dS} = -q\frac{dV}{dS}.$$

This condition is satisfied if we take $\frac{V}{\phi} = \frac{\beta}{q}$ everywhere.

Hence $$\frac{G}{v} = \frac{\beta}{q} \text{ also.}$$

But v is equal and opposite to the actual velocity of the particle and G is the gradient of potential $-\frac{dV}{dx}$ in the undisturbed part of the field. Hence if c be the current per unit area in this part we obtain

$$c = \frac{1}{R}\frac{dV}{dx} = \frac{G}{R},$$

and therefore $$-v = \frac{qRc}{\beta}.$$

The radial voltage at the particle ζ is q/capacity per unit area $= q\frac{4\pi\delta}{K}$, where δ is the double layer thickness and q the charge per unit area of the particle.

Also as before

$$\beta u_0 = \eta\frac{du}{dr} = \eta\frac{u_0}{\delta},$$

whence $$-v = \frac{KRC}{4\pi\eta}\zeta,$$

identical with the endosmotic equation but with reversed sign.

On applying this equation to a small spherical particle of olive oil in an emulsion, McLewis (*loc. cit.*; *Zeit. Koll.* IV. 211, 1909) found $\zeta = 0·05$ volt.

No— $$\zeta = \frac{q4\pi\delta}{K}.$$

If r be the radius of the particle and ϵ the total charge then

$$\epsilon = 4\pi r^2 q \text{ or } q = \frac{\epsilon}{4\pi r^2} \text{ and } \zeta = \frac{4\pi\delta\epsilon}{4\pi r^2 K} = \frac{\delta\epsilon}{Kr^2},$$

the radius of the particle was found to be 4×10^{-5} cm., δ was assumed equal to 5×10^{-8} cms., hence the total charge was 4×10^{-4} E.S.U.

For colloidal platinum a somewhat smaller value was obtained for the total charge, viz. 8×10^{-5} E.S.U.

It will be noted that in the derivation of the transverse potential difference ζ the product ηv should be constant for the same system under uniform conditions. A change in η can be produced most conveniently by alteration of the temperature. Burton (*Physical Properties of Colloidal Solutions*, p. 145) gives the following data for colloidal silver solutions in support of the validity of the equation.

°C.	$v \times 10^5$	$\eta \times 10^3$	$\eta v \times 10^7$
3	15·1	16·21	24·5
9·9	18·6	13·30	24·7
11	19·6	12·82	25·1
21	25·5	9·92	25·0
31	30·1	7·97	24·0
40·5	37·2	6·577	24·5

Burton has likewise investigated the effect of the medium on the mobility and on the transverse potential fall since these should be dependent both on the viscosity and on the specific inductive capacity; as typical of the results obtained the following may be cited:

Suspension	Water	Methyl alcohol	Ethyl alcohol	Ethyl malonate
	S.I.C. 80	33	25·8	10·6
Platinum ...	$v \times 10^5$ 20·3	—	—	2·3
	ζ −0·031	—	—	−0·054
Gold ...	$v \times 10^5$ 21·6	—	—	1·7
	ζ −0·033	—	—	−0·033
Lead ...	$v \times 10^5$ 12·0	22·0	4·5	—
	ζ +0·018	+ 0·044	+0·023	—

In the following table are inserted a few typical values for the mobility in cms. per sec. per volt per cm. (v) and the transverse potential fall ζ for various particles in aqueous solution.

Substance	$v \times 10^5$	ζ
Hydrocarbon oil ...	−43·0	−0·060
Aniline	−31·1	−0·043
Chloroform	−10·0	−0·014
Lycopodium	−25·0	−0·035
Prussian blue ...	−40·0	−0·056
Gold	−21·6	−0·030
Silver	−23·6	−0·033
Globulin in NaOH ...	+ 7·7	+0·100
" " H_2SO_4 ...	−18·5	−0·026
Lead	+12·0	+0·017
Arsenious sulphide ...	−22·0	−0·031

11. Electrification at gas-liquid interfaces.

Lenard (*Wied. Ann.* XLVI. 584, 1892) showed that a stream of atomised water when allowed to impinge on an insulated metal plate imparted a positive charge to the plate. The water drops were in consequence positively charged on atomisation leaving a negative charge in the surrounding gas. The existence of such electrification at gas-liquid interfaces has likewise been demonstrated by McTaggart (*Phil. Mag.* XXVII. 297, 1914; XXVIII. 367, 1914), who showed that gas bubbles in water underwent electric cataphoresis towards the anode, i.e. the charge on the interior or air surface of the bubble was negative leaving a positive charge in the mobile double layer in the water. There thus exists at a gas-liquid interface a transverse potential fall or electrokinetic potential and we must consider how much electrification is brought about. More recent experiments by Alty have indicated that the electrification is independent of the nature of the gas, helium, nitrogen and oxygen giving similar results and that in pure water no electric cataphoresis occurs and consequently no electric double layer exists. Thus the observations of Lenard and those of McTaggart on atomisation and electric cataphoresis respectively are due to the presence of small quantities of electrolytes in the water, in all probability alkali from the glass.

The experiments of McTaggart indicate that bubbles normally negative on the air side and positive on the aqueous side of the interface could be brought to the isoelectric point by the addition of hydrochloric acid and actually reversed in sign by the addition of tri- and tetravalent cations such as lanthanum and thorium. The addition of aliphatic alcohols which are strongly adsorbed at the air-water interface diminished very considerably the rate of migration. In discussing the effect of electrolytes on the surface tension of water we noted that they, in general, produced an elevation of σ denoting a negative adsorption or a surface concentration less than the bulk concentration. Langmuir assumes that the surface film is but one layer of molecules thick and that this film consists of pure water. McTaggart's explanation of the formation of the electric double layer by the selective adsorption of ions is evidently at variance with this assumption. It is extremely unlikely that electrolytes undergo positive adsorption in the very dilute concentrations employed by McTaggart and Alty but that the reverse is the case in the interface at the higher concentrations where their influence on the surface tension of water has been determined.

McTaggart has likewise observed some very curious effects when a bubble undergoes cataphoresis in water which is not saturated with the gas.

He found for example that a bubble which moved with a high velocity and was negatively charged in a very dilute solution of thorium nitrate gradually moved more slowly as it became smaller, passed through the isoelectric point and finally reversed its sign. Apparently the diminution in size was accompanied by a diminution in the negative charge, but the number of positive ions in the interface remained constant.

Instead of employing a cataphoretic method for determining the electrokinetic potentials at air-liquid interfaces, even more valuable information may be obtained by measurement of the E.M.F. of a cell of the type

$$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 n\text{-KCl} \mid \underset{A}{\text{solution}} \,\vdots\, \underset{\text{gap}}{\text{Air}} \,\vdots\, \underset{B}{\text{solution}} \mid n\text{-KClHg}_2\text{Cl}_2 \mid \text{Hg}.$$

This method for evaluating ΔV superior to the electrokinetic bubble method of McTaggart and Alty, or to employing a filter paper soaked

in the solution in question due to Kohlrausch, Ayrton and Perry, has been developed by Bichat and Blondlot (*Jour. de Physique* (2), II. 548, 1883), Kenrick (*Zeit. Phys. Chem.*, XIX. 625, 1896) and Frumkin (*ibid.* CIX. 34, 1924; CXI. 190, 1924).

The experimental apparatus consists essentially of a narrow vertical glass tube down the inner surface of which one liquid is made to flow, the other liquid emerges from a fine glass tip in the form of a narrow jet down the axis of the tube. The two solutions are connected with calomel electrodes employing potassium chloride or nitrate as junction liquids. The E.M.F. of the cell is measured by means of a sensitive quadrant electrometer. The greatest source of error in the method is the elimination of or the calculation of the exact values of the liquid-liquid junction potentials in the system. For electrolytes which are not very capillary active, the possible error may amount to as much as fifty per cent. of the observed E.M.F.

In spite of this apparent latitude, however, the following conclusions may be drawn from the measurements, in which distilled water or dilute sulphuric acid was used as reference liquid (solution B).

Electrolytes.

With the exception of the alkaline hydroxides NaOH, KOH and possibly the fluorides KF, NaF, the direction of the E.M.F. indicates that all monovalent anions are repelled from the free surface of waters less than the cations $Li^{\cdot}, Na^{\cdot}, K^{\cdot}, Cs^{\cdot}$. Divalent ions show on the other hand only slight differences. As has already been noted the fact that the surface tension of water is raised by the addition of salts indicates that repulsion of the salt as a whole from the surface must take place.

So far as can be ascertained from the data the behaviour of the cations $Li^{\cdot}, Na^{\cdot}, K^{\cdot}, Cs^{\cdot}$ is the same, the specific differences appear to lie in the nature of the anions. At the same concentrations these cause E.M.F.'s in the order

$$CNS' > ClO_4' > I' > MnO_4' > NO_3' \gtrsim CNO' > Br', \quad BrO_3' > CN' > Cl' > OH', F',$$

thus the extent to which the anions are repelled from the surface

decreases as we pass from right to left in this series. In agreement with this it is found that the extent to which potassium salts at normal concentrations raise the surface tension of water, falls as we pass from KF to KBr in the following manner:

Salt	$\Delta\sigma$ for normal concentration
KF ...	1·83
KCl ...	1·46
KNO_3 ...	1·12
KBr ...	1·06

In the case of KCNS the surface tension is actually lowered so that the CNS′ is apparently actually attracted to the free surface, in agreement with the observation on the large electromotive force.

The general distribution of ions on the free surface may be represented as

$$\overset{-}{\mathrm{Cl}} \quad \overset{-}{\mathrm{Cl}}$$
$$\overset{+}{\mathrm{K}} \quad \overset{+}{\mathrm{K}}$$

the free surface possessing a net negative charge.

The monobasic acids all show a more marked E.M.F than the corresponding salts. They also lower the surface tension of water. The anions appear therefore to approach nearer to the surface in the presence of H˙ ions than K˙ ions. In KOH the E.M.F. is reversed, the K˙ being less repelled from the surface than the OH′. Ammonium salts behave like potassium salts except that ammonia is quite different to the other bases, giving a strong reversed E.M.F. and lowering the surface tension of water like an organic compound.

It may be noted that similar lyotropic series for the anions have been observed at other interfaces in addition to the air-water interface. Beutner's series (see p. 249) for the oil-water interface adsorption is

$$\mathrm{CNS}' > \mathrm{I}' > \mathrm{NO_3}', \quad \mathrm{Br}' > \mathrm{Cl}' > \mathrm{SO_4}'',$$

and Gouy (see p. 212) obtained the adsorption at a neutral mercury surface, the order

$$\mathrm{HS}' > \mathrm{I}' > \mathrm{CNS}' > \mathrm{CN}' > \mathrm{Br}' > \mathrm{NO_3}' > \mathrm{Cl}' > \mathrm{OH}'.$$

Ions such as S″, HS′, I′ and CN′ are probably somewhat displaced owing to the "chemical" attraction they exert for mercury.

More recently Guyot (*Ann. d. Phys.* (10), II. 501, 1924) and Frumkin (*Zeit. Phys. Chem.* CXV. 485, 1925) have elaborated an improved method of determining the alteration in the air-liquid potential difference on the addition of capillary active materials. Instead of adopting Kenrick's method of two columns of flowing liquids only one stationary liquid surface is employed. As the other electrode a small gas flame or preferably a platinum wire coated with a radio active material is used. The ionisation of the air round the gas jet or radioactive material is sufficient to enable accurate determinations of the potential difference between this air electrode and the liquid. On account of the somewhat marked convection currents caused by the flame the radioactive deposit on the platinum wire is to be preferred as air electrode. Frumkin has extended this method to a variety of capillary active organic compounds such as the fatty acids and alcohols including the long chain insoluble compounds examined by Langmuir and Adam. Although this method has not yet been developed the results already obtained indicate that this is a powerful weapon with which the vexed question of the polarity of organic compounds might be attacked.

Non-electrolytes.

In the case of molecules which do not dissociate, the electromotive force must be due to the orientation of the molecules in the surface layer, which molecules must have a definite electric moment. In the few cases where the electromotive force can be accurately compared with the surface concentration such as *n*-butyric, *n*-valeric and *n*-caproic acids, the E.M.F. is almost approximately proportional to the surface concentration Γ, as would be the case if the moment μ of a molecule were independent of the proximity of its neighbours.

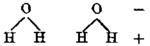
If the molecules be imagined as arranged in a parallel layer the electric moment of each molecule may be calculated from the observed potential difference. If the surface concentration be Γ we obtain $V = 4\pi N\Gamma\mu$, whence $\mu = \frac{V}{4\pi N\Gamma}$. For *n*-butyric acid it is found that $V = 0.349$ volts or 1.16×10^{-3} E.S.U. when the bulk con-

centration of the acid is 0·758 molar. From surface tension measurements the value of $4\pi N\Gamma$ is found to be $3{\cdot}79 \times 10^{15}$ whence the moment of the butyric acid molecule is $\mu = 0{\cdot}305 \times 10^{-18}$ as compared with a value of *ca.* $\mu = 2{\cdot}0 \times 10^{-18}$ calculated from the refractive index (see Gans, *Ann. Physik,* LXIV. 481, 1921; Smyth, *Phil. Mag.* XLV. 849, 1923; *J.A.C.S.* XLVI. 2153, 1924). The agreement is satisfactory when the somewhat empyric nature of the method of Gans and Smyth is considered. If the moment be considered as due to a unit charge separated from another by a distance δ, then $\mu = \epsilon\left(\frac{\delta}{K}\right)$ where K is the dielectric constant. Since $\epsilon = 4{\cdot}77 \times 10^{-10}$ E.S.U. we obtain with unit dielectric constant ($K = 1$), a value of 6×10^{-10} cms. for δ, a value in close agreement with that determined by Gouy for the double layer thickness for capillary active substances at a water-mercury interface. Performing a similar calculation for alcohol molecules we find that $\delta = 4{\cdot}8 \times 10^{-10}$ cms. It is also interesting to note that Frumkin's data would lead one to expect, contrary to the conclusions of Smyth, that the hydrocarbon chain possesses no electric moment. The following figures show the close agreement in the interfacial potentials of various acids at identical surface concentrations:

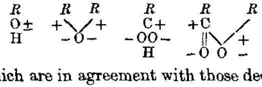
Acid	Bulk concentration mols. per litre	$RT\Gamma$	V in millivolts
n-Butyric acid ...	0·758	12·35	349
n-Valeric acid ...	0·132	12·45	355
n-Caproic acid ...	0·195	12·60	353

The limiting values of V for a completely packed surface acquires a characteristic value for various compounds. Thus V_∞ for the alcohols is 380 m.v., for the ethers $V_\infty = 550$ m.v., the surface being charged positively for these compounds. V_∞ for the higher fatty acids is identical with that of the alcohols, the esters again causing a rise in the value. Thus substitution of an organic group in the place of a hydrogen atom causes an elevation in the potential, a value being obtained which is independent of the length of the chain introduced.

Water is probably feebly polar and may be imagined to orientate itself in the form

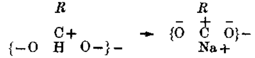


whilst the alcohols, ethers, acids and esters may be diagrammatically represented as follows:



orientations which are in agreement with those deduced from other considerations (see Chapters II and III).

In the case of salts of organic acids the positive charge falls and may even go over to a negative value, the total negative effect of a $\overset{-}{CO_2}\overset{+}{Na}$ must thus exceed that of a $\overset{-}{CO_2}\overset{+}{H}$ group. A representation in a manner somewhat as follows would indicate a mechanism by which such a change could be produced:



Introduction of a chlorine atom into the organic radical reduces the positive charge and may actually produce a negative value, thus we obtain

Compound	V_∞ in M.V.
Acetic acid	+285
Monochlor acetic acid	−150
Dichlor acetic acid	−280
Trichlor acetic acid	−600
Alcohol	+380
Ethylene monochlor hydrin ...	− 30
Ethyl acetate	+610
Ethyl monochlor acetate ...	+410

Evidently the alteration of the V_∞ values with introduction of chlorines cannot be attributed to its effect on the alteration of the strengths of the substituted acetic acids, for alcohols and esters exhibit similar changes. In order to examine the moment of the C—Cl union, some idea of the nature of its orientation at a water-air interface must be obtained.

Frumkin has obtained the following data for the effect of normal solutions of the following salts on the surface tension of water:

Salt	$\Delta\sigma$
Na acetate	+0·4
Na monochlor acetate ...	+0·1
Na dichlor acetate ...	−1·9
Na trichlor acetate ...	−7·2

Surface adsorption thus increases with the introduction of chlorine atoms or energy is required to pull a chlorine atom from the surface to the interior.

We may conclude that trichlor acetic acid is orientated as follows:

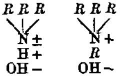
Cl
Cl Cl−
C+
———————
C+
{O H O}−

That the chlorine is negative respective to the carbon may be shown in the case of chloroform, but both methyl iodide and ethyl iodide were found to be too insoluble and volatile to give any definite values.

The iodo and brom acetic acids gave similar results to the chlor derivatives.

The value of V_∞ for triethylamine ($V_\infty = +630$ m.v.) appears to be identical with that for ammonia and the various substituted ammonias; substitution thus appears to exert no effect on the moment of this molecule.

Thus we may depict its orientation as follows:



where R may be an alkyl group or a hydrogen.

The potential is raised for compounds of the type NR_4OH which may be represented as indicated above.

12. Electrification at liquid-liquid interfaces.

Diffusion Potentials.

In a cell of the type

$$\begin{array}{c|c|c|c} M & \underset{c_1}{MX} & \underset{c_2}{MX} & M \\ & V_1 & V_2 & V_3 \end{array}$$

we note that the total electromotive force of the cell is the algebraic sum of three potential differences or

$$V = V_1 + V_2 + V_3.$$

The two electrode potentials V_1 and V_3 are according to the Nernst conception of electrolytic solution pressure given by the expression

$$V_1 = \frac{RT}{nF} \log \frac{P}{c_1},$$

where c_1 is the activity of the n-valent M ion in the first electrolyte, and

$$V_3 = \frac{-RT}{nF} \log \frac{P}{c_2},$$

thus
$$V_1 + V_3 = \frac{RT}{nF} \log \frac{c_2}{c_1}.$$

Since the observed electromotive force of the cell is V,

$$V_2 = V - \frac{RT}{nF} \log \frac{c_2}{c_1}.$$

The diffusion potential V_2 can be calculated in the following manner due to Nernst (*Zeit. Phys. Chem.* II. 611, 1888; IV. 129, 1889).

$$\begin{array}{c|c} M^{\cdot} & M^{\cdot} \\ X' & X' \\ c_1 & c_2 \end{array}$$

If we imagine that F coulombs of electricity be transported across a boundary separating two solutions of a monovalent electrolyte MX of concentrations c_1 and c_2, the electrical work performed will be V_2F, where V_2 is the difference of potential between the two solutions.

A fraction $\frac{u}{u+v}$, where u is the mobility of the cation and v the mobility of the anion, of the total current is carried by the cation

and a fraction $\frac{v}{u+v}$ by the anion. The fraction $\frac{u}{u+v}$ of cation is transported from a solution of concentration c_1 to that of c_2, whilst the fraction $\frac{v}{u+v}$ is transported in the opposite direction. The net osmotic work that must be performed by the transportation of cation and anion in this manner is thus

$$RT\frac{u}{u+v}\log\frac{c_2}{c_1} - RT\frac{v}{u+v}\log\frac{c_2}{c_1},$$

or

$$RT\frac{u-v}{u+v}\log\frac{c_2}{c_1}.$$

The electrical work and osmotic work both performed in a perfectly reversible manner are equal, thus

$$V_2F = RT\frac{u-v}{u+v}\log\frac{c_2}{c_1},$$

$$\therefore \; V_2 = \frac{RT}{F}\,\frac{u-v}{u+v}\log\frac{c_2}{c_1}.$$

For large values of the difference between the mobility of the cation and that of the anion, the diffusion potential V_2 will by no means be negligible. Both hydrogen and hydroxyl ions possess exceptionally large mobilities in aqueous solution and thus diffusion potentials between solutions of different concentrations of both acids and alkalis may assume large values as indicated by the following data for the values of V_2 between solutions of electrolytes of concentration ratios 10 : 1.

Electrolyte	u	v	V_2 in millivolts
HCl ...	318	65·4	+37·8
NaOH ...	43·55	174	−34·6
KCl ...	64·67	65·44	− 0·4
NH_4NO_3 ...	64	61·78	+ 1·1

It will be noted that liquid junction diffusion potentials can be eliminated almost completely by ensuring that the bulk of the current is carried by cations and anions possessing equal mobilities, e.g. KCl or NH_4NO_3. Thus by inserting a saturated solution of

either of these salts between any other pair of solutions forming a junction, the liquid junction potential can be greatly reduced.

The more general problem of the magnitude of the liquid junction existing between the followiug types of ionic solutions

$$\frac{M^{\cdot}c_1}{X'c_1}\Big|\frac{M^{\cdot}c_2}{Y'c_2} \quad \frac{M^{\cdot}}{X'}\Big|\frac{N^{\cdot}}{X'} \quad \text{and} \quad \frac{M^{\cdot}}{X'}\Big|\frac{N^{\cdot}}{Y'}$$

has been investigated by Planck (*Wied. Ann.* XL. 561, 1890); Johnson (*Ann. der Physik*, XIV. 995, 1904); G. N. Lewis (*J.A.C.S.* XXXI. 363, 1907); Henderson (*Zeit. Phys. Chem.* LIX. 118, 1907; LXIII. 325, 1908) and Bjerrum (*Zeit. f. Elektrochem.* XVII. 391, 1911).

If the two electrolytes of concentration c_1 and c_2 are monovalent and the ionic mobilities u_1, v_1 and u_2, v_2 respectively, then

$$V_2 = \frac{RT}{F}\log \xi,$$

where ξ is defined by the relationship

$$\frac{\xi c_2 u_2 - c_1 u_1}{c_2 v_2 - \xi v_1 c_1} = \frac{\log \frac{c_2}{c_1} - \log \xi}{\log \frac{c_2}{c_1} + \log \xi} \cdot \frac{\xi c_2 - c_1}{c_2 - \xi c_1}.$$

In those cases where $c_1 = c_2$ we find $\xi = \frac{u_1 + v_1}{u_2 + v_2}$, and since the conductivities of solutions are proportional to the ionic mobilities at dilutions of equal dissociation, we find that for strong and equally dissociated electrolytes the following:

$$V_2 = \frac{RT}{F}\log\frac{u_1+v_1}{u_2+v_2} = \frac{RT}{F}\log\frac{\lambda_{\infty_1}}{\lambda_{\infty_2}} = \frac{RT}{F}\log\frac{\lambda_1}{\lambda_2}.$$

As an indication of the magnitudes of such diffusion potentials the following values may be given:

Electrolyte function		V_2 in millivolts
HCl ...	KCl	+26·8
NaOH ...	NaCl	−17·3
NaCl ...	KCl	− 4·4
NH_4NO_3 ...	KCl	0·6

It is clear that in junctions which are sharp and well defined, the transport from one liquid to another will take place by means

of only one kind of cation and one anion, but where the junctions are diffuse and a relatively gradual conversion from one pure electrolyte to the other occurs, the transport ratio will be fluctuating from one extreme value to the other and the above equation of Planck developed on the assumption of a sharp and well-defined boundary will not be rigid. Henderson and Cumming (*loc. cit.*) have investigated this second type of boundary. For two monovalent electrolytes of concentrations c_1 and c_2 and ionic mobilities u_1, v_1 and u_2, v_2, Henderson's equation reduces to the following:

$$V_2 = \frac{RT}{F} \frac{(u_1 c_1 - v_1 c_1) - (u_2 c_2 - v_2 c_2)}{(u_1 c_1 + v_1 c_1) - (u_2 c_2 + v_2 c_2)} \log \frac{u_1 c_1 + v_1 c_1}{u_2 c_2 + v_2 c_2},$$

which undergoes still further simplification when $c_1 = c_2$,

$$V_2 = \frac{RT}{F} \frac{(u_1 - v_1) - (u_2 - v_2)}{(u_1 + v_1) - (u_2 + v_2)} \log \frac{u_1 + v_1}{u_2 + v_2}$$

or

$$V_2 = \frac{RT}{F} \frac{(u_1 - u_2) - (v_1 - v_2)}{(u_1 - u_2) + (v_1 - v_2)} \log \frac{u_1 + v_1}{u_2 + v_2}.$$

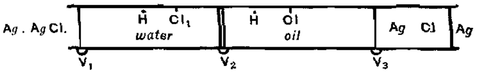
This equation is evidently identical with that of Planck only when $u_1 = u_2$ or $v_1 = v_2$, i.e. the two electrolytes contain a common or an equimobile ion.

Diffusion or liquid junctions are thus not clearly defined since the potential difference is dependent on the sharpness of the junction. Uniformly sharp junctions have been obtained by Lamb and Larson (*J.A.C.S.* XLII. 229, 1920) by allowing one liquid to flow against the other, whilst Bjerrum (*Zeit. f. Elektrochem.* LIII. 428, 1905), has obtained a relatively diffuse junction by the insertion of a sand diaphragm between the two electrolytes.

A similar phenomenon is to be noted in the case of the interface between two immiscible liquids, e.g. oil and water, owing to the unequal distribution of the ions of a dissolved electrolyte between the two media (see Nernst and Riesenfeld, *Ann. der Physik* (4), VIII. 600, 1902; Haber, *ibid.* (4), XXVI. 927, 1908; Haber and Klemensiewicz, *Zeit. Phys. Chem.* LXVII. 385, 1909; Michaelis, *Dynamik der Oberflächen*, 1909; Beutner, *Die Entstehung elektrischer Ströme in lebenden Geweben*, 1920).

The existence of the liquid potential at a liquid-liquid interface can be demonstrated in the following way.

An electrolyte, e.g. HCl is shaken up with the two immiscible solvents, water and oil, until the partition equilibrium is arrived at.



If a hydrogen electrode be immersed in each solution since the ystem is in equilibrium, the potential difference between these electrodes must be zero. Similarly for the chlorine ion, there will be a zero potential difference between two silver-silver chloride electrodes immersed in the two media.

The P.D. of a hydrogen electrode immersed in a solution of hydrogen ion activity $C_{\dot{H}}$ is given by the expression

$$V = \frac{RT}{nF} \log \frac{C_{\dot{H}}}{C_{O\dot{H}}},$$

where $C_{O\dot{H}}$ is the hydrogen ion activity of a solution for which zero potential difference exists, corresponding to the electrolytic solution pressure of the ion in that particular medium.

In the absence of an interfacial potential difference between the *two media we obtain as the* E.M.F. *of the cell*

$$V = \frac{RT}{nF} \log \frac{C_{\dot{H}a}}{C_{O\dot{H}a}} - \frac{RT}{nF} \log \frac{C_{\dot{H}b}}{C_{O\dot{H}b}},$$

where the suffixes a and b refer to the two media.

Since $V=0$ at equilibrium $\frac{C_{\dot{H}a}}{C_{\dot{H}b}} = \frac{C_{O\dot{H}a}}{C_{O\dot{H}b}}$.

Similarly for the chlorine ions $\frac{C_{Cla}}{C_{Clb}} = \frac{C_{OCla}}{C_{OClb}}$.

The partition coefficient of either ion should thus be independent of that of the other. This is evidently not the case since the partition coefficient of electrolytes containing a common ion, e.g. the chlorine ion, varies with the nature of the cation, thus the oil-water ratio for aniline hydrochloride is much greater than that for sodium chloride.

In general the interfacial potential difference will be finite and equal to

$$V_H = \frac{RT}{nF}\left(\log \frac{[C_{\dot{H}a}]}{C_{\dot{H}b}} + \log \frac{C_{O\dot{H}b}}{C_{O\dot{H}a}}\right)$$

$$= \frac{RT}{nF}\log \frac{C_{\dot{H}a}}{C_{\dot{H}b}} + L$$

where L is a constant.

The partition coefficient of one ion, e.g. the hydrogen considered as distributing itself between the two media independently of the other, is given by the expression $\frac{C_{O\dot{H}a}}{C_{O\dot{H}b}}$, which is the limiting distribution which the hydrogen ion attempts to establish but is prevented from doing so owing to the presence of the other ion in general possessing a different partition coefficient.

Beutner (*loc. cit.*) has studied numerous cells, generally of the type reversible with respect to one ion, e.g. the $Na^{\cdot}$ in the following:

$$\begin{array}{c|c|c||c|c||c|c|c} \text{Calomel} & \text{KCl} & \text{Na}X & \text{Na}X & \text{NaCl} & \text{NaCl} & \text{KCl} & \text{Calomel} \\ & \text{sat.} & \text{in water} & \text{in oil} & \text{in oil} & \text{in water} & \text{sat.} & \\ & & V_1 & & a & V_2 & & \end{array}$$

or the chlorine ion:

$$\begin{array}{c|c||c|c||c|c} \text{Calomel} & Y\text{Cl} & Y\text{Cl} & \text{NaCl} & \text{NaCl} & \text{Calomel} \\ + & \text{in water} & \text{in oil} & \text{in oil} & \text{in water} & - \\ & c_1 \quad V_1 & c_2 & c_3 & V_2 \quad c_4 & \\ & & b & & & \end{array}$$

In each cell there are two phase boundaries ‖ giving rise to interphase potentials owing to unequal ionic distribution. The E.M.F. of such a cell is consequently given by the potential

$$V = V_1 - V_2$$

if the small potential differences a or b be neglected.

In the second cell, if the chlorine ion concentrations in the four phases be $c_1\, c_2\, c_3\, c_4$ we obtain

$$V_1 = \frac{RT}{F}\log\frac{c_2}{c_1} + L,$$

$$V_2 = \frac{RT}{F}\log\frac{c_3}{c_4} + L,$$

$$\therefore\ V = V_1 - V_2 = \frac{RT}{F}\log\frac{c_2}{c_1}\frac{c_4}{c_3}.$$

In one experiment of Beutner, guaiacol was used as immiscible solvent, $\frac{N}{10}$ aniline hydrochloride and $\frac{N}{10}$ sodium chloride as electrolytes, assumed to be completely ionised in aqueous solution. The partition coefficient of these electrolytes in the guaiacol being determined by the increase in the specific conductivity of the solution after shaking with the aqueous electrolyte.

The specific conductivity of the guaiacol before contact was found to be 0·1 gemhos, after contact with the $\frac{N}{10}$ NaCl 1·3 gemhos, an increase of 1·2 gemhos. With $\frac{N}{10}$ aniline hydrochloride, the conductivity rose to 10·3 gemhos. Inserting these values as representative of the concentrations of the chlorine ions in the various solutions we obtain

$$\frac{c_4}{c_1} = \frac{0 \cdot 1}{0 \cdot 1} = 1,$$

$$\frac{c_2}{c_3} = \frac{10 \cdot 3 - 0 \cdot 1}{1 \cdot 2} = \frac{10 \cdot 2}{1 \cdot 2} = 8 \cdot 5,$$

$$\therefore \ V = 0 \cdot 058 \log 8 \cdot 5 = 0 \cdot 056 \text{ volt},$$

whilst the observed value was found to be 0·059 volt.

A closer agreement is scarcely to be expected since no correction has been made for the concentration potential b and the conductivity ratio of the two solutions is only an approximate measure of the chlorine ion concentrations, which in turn are not identical with their activities.

The following figures indicate the close agreement between the observed and calculated values when various electrolytes are substituted for the aniline hydrochloride. The effect of increasing oil solubility of the cation is clearly marked:

Salt $\frac{M}{10}$ concentration	E.M.F. obs.	E.M.F. calc.
$MgCl_2$	−·091	−0·043
KCl	+·011	+0·012
$C_6H_5NH_3Cl$ ...	+·059	+0·056
$C_6H_5N(CH_3)_2HCl$	+·091	+0·100

Various modifications of these cells have been investigated by Beutner (*loc. cit.*), Haber (*loc. cit.*), Cremer (*Zeit. f. Biol.* XLVII. 1, 1906) and others which have many important applications in biology. (Loeb and Beutner, *Biochem. Zeit.* LI. 288, 300, 1913.)

If aqueous solutions containing an electrolyte MX in two different concentrations c_1, c_2 be separated by an oil layer, the maximal voltage of the cell regarded as a concentration cell in respect to one ion will be given by the expression

Water	Oil	Water
MX		MX
c_1		c_2

$$V = \frac{RT}{F} \log \frac{c_1}{c_2},$$

whilst the minimum value will be $V = 0$.

In general the E.M.F. of the cell will be between these values since the potential difference between the oil-aqueous phases will possess a certain finite value.

If the ionic concentration at the interface to the liquid c_1 be $c_{1,\text{oil}}$ and at c_2 be $c_{2,\text{oil}}$, the potential difference of the cell will be

$$V = \frac{RT}{F} \log \frac{c_1}{c_2} \cdot \frac{c_{2,\text{oil}}}{c_{1,\text{oil}}}.$$

When $c_{2,\text{oil}} = c_{1,\text{oil}}$, i.e. when the concentration of the common ion *is uniform throughout the whole of the oil, the potential difference* is a maximum, whilst when the ions obey the partition law

$$\frac{c_1}{c_{1,\text{oil}}} = \frac{c_2}{c_{2,\text{oil}}},$$

the total E.M.F. *is zero.*

To establish the conditions of uniform ionic concentration throughout the oil, the ionic concentration of the reversible ion in the oil *must be independent of the concentration of the ion in the aqueous* phases. Partial realisation of this state of affairs has been obtained by Beutner (*loc. cit.*) utilising salicylaldehyde as non-aqueous phase. The aldehyde contains small quantities of acid which reacts with the potassium chloride

$$KCl + C_6H_4\begin{matrix}\diagup OH \\ \diagdown COOH\end{matrix} \rightarrow C_6H_4\begin{matrix}\diagup OH \\ \diagdown COOK\end{matrix} + HCl.$$

On solution in the aldehyde the two acids salicylic and hydro-

chloric are comparable in strength, hence for dilute aqueous solutions of potassium chloride the potassium ion concentration in the aldehyde depends entirely on the quantity of salicylic acid in the salicylaldehyde and the relative strengths of the two acids in this solvent. With more concentrated aqueous solutions the potassium ions present in the aldehyde will be in combination not only with salicylate ions, but with chlorine ions as well, thus promoting an interfacial potential difference. It is to be anticipated that with increasing concentrations of chloride in the aqueous phases the E.M.F. of the cell will gradually fall, an anticipation verified by experiment.

c_1	c_2	Max. E.M.F. calc.	E.M.F. obs.
$\frac{N}{2}$	$\frac{N}{10}$	·041	·021
$\frac{N}{10}$	$\frac{N}{50}$	·041	·025
$\frac{N}{50}$	$\frac{N}{250}$	·041	·034
$\frac{N}{250}$	$\frac{N}{1250}$	·041	·041

If the oil-insoluble chlorine ion be replaced by the oil-soluble salicylate ion in the aqueous phases, the concentration of the electrolyte in the oil phase will not be independent of the concentration in the aqueous phase, but a normal partition coefficient will be obtained with concomitant interphase potential.

Evidently the non-aqueous phase may possess acidic or basic characters either in virtue of its own properties, e.g. nitrobenzene and aniline, or through the addition of small quantities of soluble acidic or basic substances, e.g. salicylic acid to salicylaldehyde or methylamine to nitrobenzene.

It is thus possible to arrange the various non-aqueous media in a series with the aid of a cell of the type

Calomel	MX in H_2O c	non-aqueous phase I	non-aqueous phase II	MX in H_2O c	Calomel

in which the E.M.F. actually measured is the difference in the

potentials between the two non-aqueous phases and aqueous solutions containing the same concentration of electrolytes.

Some of the values obtained by Beutner are given below. In all cases normal KCl was used as aqueous phase

C_6H_5CHO	Cresol	$-0{\cdot}13$ volt
"	Phenol	$+0{\cdot}13$ "
"	Guaiacol	$+0{\cdot}08$ "
"	Acetophenone	$-0{\cdot}07$ "

The oil solubility of various ions can be compared one with another with the aid of cells of the type

$$\begin{array}{c|c|c} \dfrac{MX}{\text{in } H_2O} & \text{Oil} & \dfrac{MY}{\text{in } H_2O} \end{array} \quad \text{and} \quad \begin{array}{c|c|c} \dfrac{MX}{\text{in } H_2O} & \text{Oil} & \dfrac{NX}{\text{in } H_2O} \end{array}$$

Utilising potassium chloride in the left-hand compartment of the cell and substituting for potassium chloride other potassium salts in the right-hand compartment of the cell, the E.M.F. of the cell rises as the anion becomes more oil soluble. Beutner (*Zeit. Electrochem.* XXIV. 94, 1918) found the following order for increasing oil solubility of the anions:

$$SO_4'' \quad Cl' \quad Br' \quad I' \quad SCN',$$

whilst for increasing oil solubility of the cations the order was

$$Mg^{\cdot\cdot} \quad Ca^{\cdot\cdot} \quad Ba^{\cdot\cdot} \quad Na^{\cdot} \quad K^{\cdot}.$$

The general order was found frequently to be independent of the nature of the oil (Baur, *Zeit. Electrochem.* XXIV. 100, 1918), especially in those cases where the oil possessed distinct acidic or basic characters.

13. Adsorption of ions at oil-water interface.

Hartridge and Peters (*Proc. Roy. Soc.* A, CI. 348, 1922) have measured the interfacial tension of liquid fatty acids and their solutions in benzene against aqueous borate, phthalate and phosphate buffer solutions of varying concentration and P_H.

In acid solution as far as $P_H = 5$ the interfacial tension is constant but with increasing alkalinity it falls. In the case of fatty acids the tension becomes vanishingly small when the P_H exceeds 8 and the acid dissolves in the alkali in the form of micelles (see Ch. IX).

The effect of alteration of the P_H on the interfacial tension is as we have seen operative on the carboxyl groups which are orientated

in the aqueous phase at the interface. The experiments of Langmuir and Adam (see Ch. III) have shown that a fatty acid occupies a 16 °/₀ larger area on acid solutions than on alkaline ones, a transition occurring abruptly from one area to the other in the neighbourhood of $P_H = 5$ where the interfacial surface tension shows the first signs of change. Hartridge and Peters suggested that the gradual change in interfacial tension was caused by the gradual substitution of sodium ions for hydrogen ions in the carboxyl groups, i.e. due to the formation of soap at the interface. Support is given to this view by application of the Gibbs' equation. The measurements with oleic acid were complicated by oxidation but the following table gives the data for a 0·098 grm. per cent. solution of palmitic acid in benzene.

Concentration of phosphate buffer	Interfacial tension in dynes/cm. at	
	$P_H = 5{\cdot}6$	$P_H = 7{\cdot}6$
0·05M	33·3	27·8
0·025M	—	27·7
0·005M	32·3	29·1
0·0005M	—	31·9

For the buffer solution $P_H = 5{\cdot}6$ the variation of interfacial tension with the strength does not exceed the experimental error, but in the more alkaline solution we must conclude that either sodium ions or phosphate ions (or both) are positively adsorbed according to the equation

$$d\sigma_{\text{PH constant}} = -\Gamma_{\text{Na}^\cdot} \, d\mu_{\text{Na}^\cdot} - \Gamma_{\text{PO}_4{}''} \, d\mu_{\text{PO}_4{}''} \quad \ldots\ldots\ldots(1)$$

Γ and μ being taken per grm. equivalent and the dividing surface being so placed that Γ for the palmitate ions is zero.

With the buffer at 0·05 m. a change from $P_H = 5{\cdot}6$ to $P_H = 7{\cdot}6$ involves a slight increase in the sodium ion potential (since the change is effected by adding caustic soda) as well as a hundredfold decrease in the hydrogen ion concentration, thus

$$d\sigma = -\Gamma_{\text{H}^\cdot} \, d\mu_{\text{H}^\cdot} - \Gamma_{\text{Na}^\cdot} \, d\mu_{\text{Na}^\cdot}. \quad \ldots\ldots\ldots\ldots\ldots(2)$$

Applying the above equations to the experimental data we find from (1) that a change of buffer from 0·05 m. to one-hundredth of

this value causes a change in the surface tension of 4·1 dynes per cm., whilst $d\mu_{Na^{\cdot}} \leqq RT \times 2{\cdot}303 \times 2$.

From (2) a change of a hundredfold in the hydrogen ion concentration or $d\mu_{H^{\cdot}} = 2{\cdot}303\, RT \times 2$ with a small positive change in *the sodium ion concentration* causes a change *in the surface tension* of 5·5 dynes per cm.

If we assume $\Gamma_{PO_4'''} = 0$ then $\Gamma_{H^{\cdot}} + \Gamma_{Na^{\cdot}} = 0$ if there be no volume charge. We thus obtain

$$-4{\cdot}1 < -\Gamma_{Na^{\cdot}}\, 2{\cdot}303\, RT \times 2,$$

$$-5{\cdot}5 > +\Gamma_{H^{\cdot}}\, 2{\cdot}303\, RT \times 2 = -\Gamma_{Na^{\cdot}}\, 2{\cdot}303\, RT \times 2.$$

The difference between 4·1 and 5·5 may be accounted for by the change in the activity coefficient of the sodium ions in the buffer with concentration. Assuming that

$$\Gamma_{Na^{\cdot}}\, 2{\cdot}303\, RT \times 2 = -\Gamma_{H^{\cdot}}\, 2{\cdot}303\, RT \times 2 = 5{\cdot}0,$$

$$\Gamma_{Na^{\cdot}} = -\Gamma_{H^{\cdot}} = 4{\cdot}5 \times 10^{11} \text{ grm. equivalents per sq. cm.}$$

This indicates that at a $P_H = 7$ about one-tenth of the number of —COOH groups have been converted into —COONa groups. It must, however, be observed that the method does not permit us to discover whether or not the groups are ionised.

14. The glass electrode.

Haber and Klemenziewicz (*Zeit. Phys. Chem.* LXVII. 385, 1909) showed that if two solutions of different P_H, into each of which a calomel electrode dips, are separated by a thin glass membrane an E.M.F. is obtained equal to $\frac{RT}{F} \times$ the difference in P_H. The glass is evidently to be considered as a solid electrolyte containing H˙ and OH′ ions at a constant thermodynamic potential which depends only on the electrical potential of the glass, as that of the mercurous ions in mercury depends only on the electrical potential of the mercury, whilst the thermodynamic potential in the aqueous phase is a function of the concentration. Hence,

$$dV = \frac{d\mu_{H^{\cdot}}}{96{\cdot}5 \times 10^{10}}.$$

The behaviour of the glass electrode has been examined in more detail by a number of investigators, notably Meyer (*Wied. Ann.*

XL. 244, 1890), Borelius (*Ann. Phys.* XLV. 929, 1914), Freundlich and Rona (*Sitz. Preuss. Akad. der Wiss.* 397, 1920), ibid. and Ettisch (*Zeit. Phys. Chem.* CXVI. 401, 1925), Hughes (*J.A.C.S.* XLIV. 2860, 1922), Horovitz (*Zeit. f. Physik,* XV. 368, 1923), Cremer (*Zeit. f. Biol.* XXIX. 562, 1908; *Zeit. Phys. Chem.* CXV. 424, 1925).

It is found that in alkaline solutions ($P_H > 11$ for soft glass) the glass no longer functions as a hydrogen electrode but is affected by an alteration in the sodium ion concentration of the solution. With sodium amalgams, in fact, glass may serve as a sodium electrode of constant thermodynamic potential.

In addition to hydrogen and sodium ions other metallic ions such as silver may be present in glasses which thus act as mixed electrodes. When equilibrium is attained between all the electromotively active ions in the glass and solution the formal relationship

$$V = \frac{RT \log C_{H^{\cdot}} - K_{g.H^{\cdot}} - K_{l.H^{\cdot}}}{96{\cdot}5 \times 10^{10}} = \frac{RT \log C_{Na^{\cdot}} - K_{gNa^{\cdot}} - K_{lNa^{\cdot}}}{96{\cdot}5 \times 10^{10}}$$

must be obeyed.

It follows that the thermodynamic potentials of the hydrogen and sodium ions in the glass must be affected by the concentrations in the solution or ionic replacement in the glass occurs. This power of ionic interchange is shared in common with glass by the naturally occurring hydrated silicates the zeolites.

15. Membrane potentials.

In the discussion on the liquid-liquid potentials it has been shown that the interposition of a layer of oil between two aqueous solutions of an electrolyte may give rise to a difference of potential between the two aqueous layers. Such cells may be reversible with respect to either ion, and may therefore be regarded as cells permeable to one ion.

The cause of the potential difference is, however, not to be attributed to ionic impermeability, but to the actual existence of two phases in which the electrolyte is dissolved and in which the partition coefficients of the two ions of the electrolyte are not identical.

There exist a number of membranes which are permeable to some ions and not to others, and these give rise to definite potential differences when the membrane is interposed between two solutions of the electrolyte. These membranes must be considered capillary in structure and selective permeability attributed to selective ionic adsorption, or in some cases to restriction imposed by the size of the capillaries.

The electrolyte is, however, dissolved in one medium only, the water; and the source of the membrane potential is attributable to the permeability of the membrane to one ion only and to no other cause.

The theory of the membrane potential has been developed by Donnan (*Zeit. f. Elektrochem.* XVII. 572, 1911) on the following lines.

A vessel is divided into two halves by means of a membrane, on one side of the membrane a solution of a salt of which both ions, e.g. $Na^{\cdot}$ and Cl', can pass through the membrane, is placed. To the other side a salt for one ion of which the membrane is permeable, and to the other impermeable, e.g. the sodium salt of congo red $Na^{\cdot}\, R'$, is added.

If it be assumed that complete electrolytic dissociation of each salt occurs, and that there are equal quantities of liquid on each side of the membrane sodium chloride will commence to diffuse from one side to the other.

We can represent diagrammatically the initial and final states of the system as follows:

$$\begin{array}{ll|ll} c_2 & Na^{\cdot} & Na^{\cdot} & c_1 \\ c_2 & Cl' & R' & c_1 \\ \multicolumn{4}{c}{\text{Initial}} \end{array} \qquad \begin{array}{ll|l} c_2-x & Na^{\cdot} & Na^{\cdot}\ c_1+x \\ c_2-x & Cl' & Cl'\ x \\ & & R'\ c_1 \\ \multicolumn{3}{c}{\text{Final}} \end{array}$$

At equilibrium, the change in free energy produced by the reversible transport of a small quantity of sodium chloride δn from one side to the other at constant temperature and volume is zero, or

$$\delta n\, RT \left\{ \log \frac{c_1 + x}{c_2 - x} + \log \frac{x}{c_2 - x} \right\} = 0,$$

or $$(c_1 + x)(x) = (c_2 - x)^2,$$

or $$x = \frac{c_2^2}{c_1 + 2c_2} \text{ or } \frac{x}{c_2} = \frac{c_2}{c_1 + 2c_2} \text{ and } \frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2}.$$

If c_2 is small compared to c_1, we obtain

$$\frac{c_2 - x}{x} = \frac{c_1}{c_2}.$$

The sodium chloride will thus distribute itself on either side of the membrane in a ratio which is a function of the concentrations of both salts.

The following table gives an idea of the magnitude of influence of the colloid on the distribution ratio of the sodium chloride:

Initial concentration of Congo red c_1	Initial concentration of sodium chloride c_2	$\frac{c_2}{c_1}$	$100\frac{x}{c_2}$	$\frac{c_2 - x}{x}$
0·01	1	100	49·7	1·01
0·1	1	10	47·6	1·1
1	1	1	33	2
1	0·1	0·1	8·3	11
1	0·01	0·01	1	99

If the concentration of the diffusible electrolyte is small, relative to that of the colloid electrolyte, only a small quantity of salt will diffuse across the membrane, whilst if the electrolyte is present in relatively large quantities, there will obtain practically an equal distribution on either side of the membrane. A similar treatment permits of the calculation of the equilibrium distribution of a salt containing no ion in common with that of the colloid electrolyte.

If pure water be placed in one compartment and the colloid electrolyte in the other, the diffusible ion will penetrate with an accompanying hydroxyl ion resulting in the formation of acid in one compartment, and alkali in the other,

$$\begin{array}{cc|c} Na^{\cdot} & R' & H_2O \\ c_1 & c_1 & \end{array} \qquad \begin{array}{cc|cc} c_1 - x & Na^{\cdot} & Na^{\cdot} & x \\ X & H^{\cdot} & OH' & x \\ c_1 & R' & & \end{array}$$

Initial Final

As before, we obtain the expression for the mass law by application of the principle of virtual work to the system in equilibrium. If (x) be the concentration of hydroxyl ions corresponding to a concentration X of hydrogen, viz.:

$$(c_1 - x)(X) = x^2.$$

If the ionisation constant of water be K_w, then $K_w = (x)(X)$, or

$$x^2 = \frac{(c_1 - x) K_w}{x},$$

or

$$x^3 = (c_1 - x) K_w.$$

For small hydrolysis where c_1 is great compared with x,

$$x^3 = c_1 K_w \quad \text{or} \quad x = \sqrt[3]{c_1 K_w}.$$

The value of K_w at ordinary temperatures is *ca.* 10^{-14} the percentage hydrolysis $100 \frac{x}{c_1}$ of the colloidal electrolyte can thus be computed from the bulk concentration and is evidently very small, e.g. for $c = 0{\cdot}01$, $100 \frac{x}{c_1} = {\cdot}05\,\%$. The insertion of the membrane thus gives rise to an unequal distribution of the electrolyte on either side, to an alteration in the apparent osmotic pressure of the colloidal electrolyte (Donnan and Harris, *J.C.S.* XCIX. 1559, 1911; Donnan and Allmand, *ibid.* CV. 1941, 1914; Donnan and Garner, *ibid.* CXV. 1313, 1919) and also to a potential difference.

The magnitude of the potential difference can be calculated by consideration of the work done in the isothermal transfer of a small quantity of electricity ($F\delta n$) from one solution to the other when equilibrium is obtained.

If $n\delta n$ mols. of $Na^{\cdot}$ are transferred from one side to the other and $(1 - n)\,\delta n$ mols. of Cl' in the reverse direction, $\frac{n}{1-n}$ being the transport values of the ions, the osmotic work done is

$$n\delta n\, RT \log \frac{c_2 - x}{c_1 + x} + (1 - n)\,\delta n\, RT \log \frac{x}{c_2 - x}.$$

The electrical work done, if V_1 and V_2 be the potentials of the solution, is $(V_2 - V_1) F\delta n$, which must be equal to the above.

We have seen that at equilibrium (p. 253)

$$\frac{c_2 - x}{c_1 + x} = \frac{x}{c_2 - x} = \lambda \text{ say},$$

hence the potential across the membrane

$$V_2 - V_1 = \frac{RT}{F} \log \frac{1}{\lambda}.$$

We have seen that $\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2}$, hence $\lambda = \frac{c_2}{c_1 + c_2}$.

The potential difference across the membrane is accordingly

$$V_2 - V_1 = \frac{RT}{F} \log \left(1 + \frac{c_1}{c_2}\right) = \cdot 058 \log \frac{c_1}{c_2}$$

for a small $c_2 : c_1$ ratio.

The magnitude of this membrane potential is discerned from the following figures:

$\frac{c_1}{c_2}$	$V_2 - V_1$
10	·058
100	·116
1000	·174
10000	·232

and potentials of this order of magnitude have been observed by Donnan and Green (*Proc. Roy. Soc.* A, XC. 450, 1914) at a copper ferrocyanide membrane.

It is evident that increasing the quantity of diffusible electrolyte in the solution decreases the membrane potential, a phenomenon observed in the case of Procter and Wilson (*J.C.S.* CIX. 1317, 1916) for tannin and by Loeb (*Jour. Gen. Physiol.* III. 607; III. 691; III. 827; IV. 33; IV. 97, 1921) (see p. 304) in the case of gelatine.

CHAPTER VIII

CONDITIONS OF STABILITY IN SUSPENSIONS AND EMULSIONS

In discussing the various methods by which dispersions such as suspensions or emulsions are formed we noted that the stability of such systems was not necessarily determined by the fact that they could be prepared. An examination of the dispersion by means of a microscope, or if the dispersion be a fine one, an ultramicroscope, reveals the fact that the small particles are in a state of lively agitation—the Brownian movement. Impact between various particles would necessarily follow from such thermal agitation and if such impact permitted the agglomeration of the particles, resulting in a decrease in the free surface energy of the system, precipitation or coagulation would ensue. In general, however, such suspensions and emulsions are stable and some factor must necessarily be operative either in preventing coalescence on collision or in reducing the number of collisions. The chief factor to be considered is the electrical charge on the suspensions and emulsions. We have already noted that electrification may result either by a process of superficial ionisation or by preferential adsorption of an ion in solution. The disperse phase is thus charged and the particles may be regarded as somewhat massive ions. On discharging the particles the forces opposing coalescence on collision are removed and coagulation results. In this chapter we shall consider the nature of the Brownian movement and the mechanism by which the charge on the particles may be reduced by various means so as to effect coagulation and precipitation.

1. The Brownian Movement.

In the seventeenth century Leeuwenhoek first noted that microscopic animalculae when suspended in water were not at rest but were in a state of rapid agitation. Nevertheless, until the investigations of Robert Brown (*Edin. Phil. Jour.* v. 358, 1828; *Phil. Mag.* IV. 161, 1828; VI. 161, 1829; VIII. 41, 1830), these movements were always associated with the ciliary agitation of

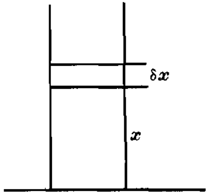
living organisms. Brown, however, examined fine suspensions of inert materials such as finely divided metals, wax, coal and many other substances and confirmed the existence of this irregular motion as a general property of fine suspensions. He likewise proved that this agitation was not caused by convectional currents in the liquid nor by disturbances which might be produced by evaporation. Experiments on the Brownian movement of small particles in liquids were continued and extended by Wiener (*Pogg. Ann.* CXVIII. 79, 1863), S. Exner (*Wien. Sitz.-Ber. Natur-Wiss.* LVI. 116, 1867), Dancer (*Trans. Manc. Phil. Soc.* 162, 1868), Jevons (*ibid.* 78, 1870), Cantori (*Nuovo Cimento,* XXVII. 156, 1867) and others without success in the elucidation of the cause of the motion. That the Brownian agitation was the result of molecular bombardment was suspected by Carbonelle in 1874, Deslaux (*Jour. Roy. Microscopic Soc.* 1877) and by Bodaszewski (*Chem. Centralblatt,* XVII. 709, 1881) who first observed similar irregular zigzag motions in the particles of smoke from burning paper and in the fog particles of ammonium chloride, but this point of view was first stated in a definite form by Gouy (*Jour. de Phys.* VII. 561, 1881; *C.R.* CIX. 102, 1889) and Ramsay (*Chem. News,* LXV. 90, 1892).

That the Brownian agitation could be regarded as nothing less than a visible proof of the kinetic theory and that the small suspended particles could be regarded for this purpose as large and visible molecules was confirmed and elaborated by the experimental work of Zsigmondy, F. Exner, Henri, Chaudesaignes, and Perrin. These investigators showed that the motions of the small particles were in experimental agreement with those that would be anticipated from an application of the kinetic theory making the basic assumption that the suspended particle may be regarded for kinetic purposes as a large molecule possessing a mean kinetic energy equal to the mean kinetic energy of a molecule of the solution in which it is suspended, the theoretical application of which has been extended in detail by Perrin, A. Einstein and v. Smoluchowski.

2. The distribution of particles in colloidal suspensions.

In a vertical cylinder of liquid containing a suspension slightly denser than the surrounding liquid in which it is dispersed we should anticipate that since the suspension particles behave exactly

in the manner which large molecules might be expected to behave, when equilibrium is attained the suspension density would be greatest at the bottom of the cylinder and least at the top establishing an exponential concentration gradient similar to the atmosphere around the globe. The following conditions of equilibrium were established by Perrin (*Les Atomes*).



Consider the equilibrium in a vertical cylinder of suspension of density ρ_1 in a suspension medium of density ρ_2 of unit cross-section and height x_0. If at a height x there are n particles per unit volume and at a height $x+\delta x$, $n+\delta n$ particles per unit volume the difference in osmotic pressures due to the particles on the assumption that the suspension conforms to the laws of an ideal solution will be

$$\frac{RT}{N}n - \frac{RT}{N}(n+\delta n) \quad \text{or} \quad -\frac{RT}{N}\delta n.$$

This difference in osmotic pressures at equilibrium exactly balances the apparent weight due to gravitational attraction of the particles in this small volume of unit cross-section. The number in the cross-section is $n\,\delta x$ and if V be the volume of each particle the apparent weight of the particles will be $n\delta x . V(\rho_1-\rho_2)g$.

Thus at equilibrium we obtain

$$-\frac{RT}{N}\delta n = -n\,\delta x\, V(\rho_1-\rho_2)g,$$

or

$$\frac{RT}{N}\log\frac{n}{n_0} = V(\rho_1-\rho_2)g(x-x_0),$$

where n and n_0 are the number of particles per unit volume at heights x and x_0 respectively.

Perrin tested this relationship with particles of gamboge and mastic dispersed in water. Gamboge emulsions are readily prepared by rubbing gamboge with a soft brush under water or by solution in alcohol and pouring rapidly into a large excess of water. The emulsions thus prepared contain particles of varying sizes but by submission to a process of fractional centrifuging an emulsion

of spherical particles reasonably uniform in diameter may be prepared.

The mean density of the emulsion particles was determined both from the specific gravity of the solid and from the specific gravity of an emulsion containing a known amount of the solid in the dispersed state, no effect due to dispersion on the apparent density could be detected.

The determination of the volume of the individual particles in the case of gamboge was effected by three different methods.

(*a*) By observation of the rate of fall of the upper surface of a dilute emulsion in a capillary tube maintained at a constant temperature the limiting velocity of fall of the particles can be determined.

According to Stokes the limiting velocity v imparted to a sphere moving through a liquid of viscosity η under a constant applied force F is given by

$$v = \frac{F}{6\pi\eta r},$$

where r is the radius of the sphere. In the case of the spherical gamboge emulsions settling under the influence of gravity

$$F = \frac{4}{3}\pi r^3 (\rho_1 - \rho_2) g,$$

or

$$r = \sqrt{\frac{9}{2}\frac{\eta v}{(\rho_1 - \rho_2) g}}.$$

Although Stokes' law does not apply to particles so small that the Brownian movement influences the rate of gravitational settling, yet for the relatively coarse emulsions prepared in this way, no sensible error is introduced.

(*b*) On acidulating a gamboge emulsion the particles are rapidly precipitated. By precipitating the particles from a known volume on to a glass coverslip the number originally contained in the volume could readily be counted with the aid of a low power microscope. From a knowledge of the total quantity of gamboge in the emulsion and the number of particles present the individual volume can readily be ascertained.

(*c*) By precipitating a sufficient number of gamboge particles on glass coverslip the length of a string of particles could be

measured and the number in the string counted, from which the radius could be deduced.

As typical of the variations in particle radius determined by these three methods the following experimental values of Perrin for gamboge emulsions may be cited:

Method	$r \times 10^{-4}$ cm.		
	(a)	(b)	(c)
Emulsion I ...	·49	—	·50
„ II ...	·45	·46	·46
„ III...	·3675	·3667	·371
„ IV ...	·213	·212	—
„ V ...	·15	·14	—

The distribution of particles in a vertical column of the emulsion was determined by Perrin with the aid of a microscope and micrometer focussing arrangement. The height of the column under the microscope was 0·1 mm. and the number at various depths was counted with the aid of the eye. The following results are typical of such determinations.

(i) Radius of gamboge particle $2{\cdot}6 \times 10^{-5}$ cm.:

Depth increment ...	0	6μ	12μ	18μ
Number	305	530	940	1880
Calculated number ...	280	528	995	(1880)

(ii) Radius of gamboge particle $1{\cdot}06 \times 10^{-5}$ cm.:

Depth increment ...	0	30μ	60μ	90μ
Number	12	22·6	47	100
Calculated number ...	11·1	23	48	(100)

The difficulty associated with such a conception of an atmospheric

concentration gradient applicable to colloidal particles is that with the rate of increase observed by Perrin over a depth of 0·1 mm. the concentration at a depth of say 1 cm. would already be enormous. In actual practice, however, the concentration has been found to approach a limiting value, and to become virtually constant after a definite maximum has been reached. This fact has led to a criticism of Perrin's work by Burton (*Proc. Roy. Soc.* A, C. 705, 1922). Burton ascribes this discrepancy to the fact that the particles are charged and consequently exert a mutual repulsion on one another. He suggests that this charge on the particles will exert a force on a unit charge equivalent to $kn\epsilon$ in the layer δx, consequently the total force on the layer of particles in the thickness δx will be $(kn\epsilon)(n\epsilon\delta x)$ or $kn^2\epsilon^2\delta x$.

Perrin's equation will thus be modified by the inclusion of this term to

$$\frac{RT}{N}\delta n + kn^2\epsilon^2\delta x = n\,\delta x\,V(\rho_1 - \rho_2)\,g.$$

Writing this in the form $A\delta n = (Cn - Bn^2)\,\delta x$ we obtain

$$n = \frac{C}{B + ke^{-\frac{C}{A}x}}.$$

Thus for large values of x, n becomes constant and equal to

$$\frac{C}{B} = \frac{V(\rho_1 - \rho_2)\,g}{ke^2}.$$

Porter and Hedges (*Trans. Farad. Soc.* XVIII. 1, 1922) criticise Burton's treatment by pointing out that the colloidal solution does not in fact contain charges all of one sign but is electrically neutral as a whole, further, that a charged colloidal particle with its attached double layer should at small distances function as an electrical doublet and thus not repel but actually attract other and similar doublets. They point out that the extension of Perrin's treatment to great depths is only possible if we replace the simple Van t' Hoff law $\pi = cRT$ obtaining in dilute solutions by the osmotic laws of concentrated solutions.

Porter makes use of the Sackur-Porter osmotic law for concentrated solutions

$$\pi = \frac{nRT}{N(1 - bn)},$$

where b corresponds to the b term in Van der Waals' equation and is proportional to the volume of the osmotically active particle together with its water of solvation, thus

$$\frac{d\pi}{dn}=\frac{RT}{N(1-bn)^2}\quad\text{.......................(1)}$$

If the osmotic pressure be a function of the hydrostatic pressure of the solution p and of the numerical concentration we have the mathematical identity

$$\frac{d\pi}{dp}=\left(\frac{d\pi}{dp}\right)_n+\left(\frac{d\pi}{dn}\right)_p\frac{dn}{dx}\cdot\frac{dx}{dp}.$$

Porter has shown (*Trans. Farad. Soc.* XIII. 123, 1917; *Proc. Roy. Soc.* A, LI. 522, 1917) $\frac{d\pi}{dp}=\frac{\rho_2-s}{\rho_2}$, where s is the shrinkage. Also

$$\frac{d\pi}{dp}=1-\frac{dp_0}{dp}=\frac{u-\sigma}{u},\quad\text{also}\quad\frac{dp}{dx}=\frac{g}{\sigma},$$

where σ is the specific volume of the solution, u that of the solvent.

Hence $$\frac{s-\sigma}{u}=\frac{\sigma}{g}\cdot\frac{d\pi}{dn}\,\frac{dn}{dx}.\quad\text{....................(2)}$$

From (1) and (2) we obtain

$$\frac{dn}{dx}=\frac{s-\sigma}{u\sigma}\,\frac{gN}{RT}(1-bn)^2.$$

If there be no contraction when gamboge and water are intermingled $\sigma=c\rho_1+(1-c)\,u$, where ρ_1 is the density of gamboge and $s=u$.

$$\therefore\ s-\sigma=c(\rho_1-u)=nm(\rho_1-u),$$

thus $$\frac{dn}{dx}=kn(1-bn)^2,$$

where $$k=\frac{gNm(\rho_1-u)}{RTu^2},$$

or $$\log_e\frac{n}{1-bn}+\frac{1}{1-bn}=kx+A.$$

This curve tends asymptotically for large values of x to the value $n_\infty=\frac{1}{b}$ and has a point of inflection for $n=\frac{n_\infty}{3}$.

The following experimental values were obtained by Porter:

x in cm. ...	·023	·033	·043	·063	·083	·103	·123	·143
$n \times 10^{-6}$ ...	·95	2·14	3·61	7·14	8·69	9·52	9·76	9·76

whilst values calculated with the aid of the above equation were, putting $b = 10{\cdot}2 \times 10^{-8}$ cm.^{3}, $k = 121$,

x in cm. ...	·024	·032	·0375	·047	·061	·089	·115
$n \times 10^{-6}$ ...	1	2	3	5	7	9	9·7

3. The Brownian movement of translation.

According to Stokes' law the limiting velocity of a spherical particle of radius r moving through a liquid of viscosity η under the influence of a force F is

$$v = \frac{F}{6\pi\eta r}.$$

If there are n particles in a unit volume of liquid then $\frac{nF}{6\pi\eta r}$ will move through a sq. cm. per second.

The force acting on a particle suspended in a solution will be caused by the osmotic pressure differences in the suspension or

$$Fn = \frac{d\pi}{dx},$$

but for dilute solutions $\pi = \frac{RTn}{N}$ or $\delta\pi = \frac{RT\delta n}{N}$,

hence $$\frac{nF}{6\pi\eta r} = \frac{RT\delta n}{N\delta x \,.\, 6\pi\eta r}.$$

If we denote the diffusion coefficient of the particles by D the quantity moving across unit area under the influence of a concentration gradient $\frac{dn}{dx}$ will be $D\frac{dn}{dx}$.

The quantity moved by diffusion will be that impelled by the difference in osmotic pressure, or

$$D\frac{dn}{dx}=\frac{RT\delta n}{N6\pi\eta r\,\delta x},$$

or

$$D=\frac{RT}{6\pi\eta r N},$$

giving us a value for the diffusion constant in terms of the temperature and viscosity of the medium and the radius of the particle. For very small particles Stokes' law is no longer exact and the departure to be expected with decreasing diameter has been investigated in some detail by Sutherland (*Phil. Mag.* VI. 1, 781, 1905), Cunningham (*Proc. Roy. Soc.* A, LXXXIII. 357, 1910), and Millikan (*Phys. Rev.* XXXII. 349, 1911).

Of the various formulae suggested, that proposed by Cunningham appears to conform most closely to Millikan's experimental values. We obtain

$$D=\frac{RT}{N6\pi\eta r}\left(1+A\frac{\lambda}{r}\right),$$

where A is a constant $=0{\cdot}815$ and λ the mean free path of a molecule of the solvent.

Einstein (*loc. cit.*) showed further that the actual mean distance $\bar{x}$ travelled by a particle in a short time t under the influence of random molecular collisions was related to the diffusion constant D, by the following equation:

$$\overline{x^2}=2Dt \quad \text{or} \quad \overline{x^2}=\frac{R}{N}\frac{Tt}{3\pi\eta r}.$$

Langevin (*C.R.* CXLVI. 530, 1908) has obtained this relationship in a relatively simple manner.

If we consider a particle of mass m moving parallel to the x axis with a component velocity $\dot{x}$ under the influence of molecular shocks the equation of motion will be

$$m\ddot{x}=-6\pi\eta r\dot{x}+\phi,$$

where ϕ is the force due to molecular collision, which is constantly varying both in magnitude and sign but nevertheless impels the particle continuously.

Then

$$m\frac{d^2x^2}{dt^2}-m\dot{x}^2=-3\pi\eta r\frac{dx^2}{dt}+\phi x.$$

For a large number of identical particles the term ϕx vanishes. Replacing $\frac{dx^2}{dt}$ by z we obtain

$$\frac{m\,dz}{2dt}+3\pi\eta r z=m\dot{x}^2.$$

Now $\frac{1}{2}m\dot{x}^2$ is the mean kinetic energy of the particle due to the component of its velocity parallel to the x axes, or

$$m\dot{x}^2=\frac{RT}{N} \text{ and } \frac{m\,dz}{2dt}+3\pi\eta r z=\frac{RT}{N}.$$

The solution of the equation is

$$z=\frac{RT}{N}3\pi\eta r+Ce^{-\frac{6\pi\eta r}{m}t}.$$

When the motion reaches a steady state

$$z=\frac{RT}{N.3\pi\eta r},$$

from which by integration we obtain

$$\bar{x}^2=\frac{R}{N}\frac{Tt}{3\pi\eta r}.$$

Independently of Einstein, Smoluchowski arrived at a similar solution to the problem of the mean displacement of a particle. He obtained

$$\bar{x}^2=\frac{32}{27}\frac{R}{N}\frac{Tt}{3\pi\eta r}.$$

4. The Brownian motion of rotation.

Not only do particles in Brownian agitation move rapidly about in the suspension medium, the magnitude of the movements being capable of exact calculation from the foregoing mathematical considerations, but they are likewise undergoing rotational motion due to an unequal distribution of molecular impacts upon the faces of the parts of a particle on each side of its axis of rotation.

The mean energy of rotation will necessarily by the laws of equipartition of energy be equal to the mean energy of translation.

Einstein (*loc. cit.*) has shown that the mobility of a system (B) referred to a parameter a is related to the mean displacement δ by the following equation

$$\delta^2=\frac{2R}{N}Tt.B,$$

where t is the time in which the alteration δ in the parameter a due to molecular bombardment has taken place.

In the case of translational motion $B = \frac{1}{6\pi\eta r}$ or $\bar{x}^2 = \frac{RTt}{N3\pi\eta r}$.

In the case of rotational motion, if a torque of moment I be applied to a sphere of radius r in a medium of viscosity η the angular velocity acquired by the sphere (see v. Kirchhoff, *Vorlesungen über Mechanik*, 26) will be $\dot{\omega} = \frac{I}{8\pi\eta r^3}$.

Hence $$B = \frac{1}{8\pi\eta r^3}.$$

Thus $$\bar{r}^2 = \frac{RTt}{N4\pi\eta r^3},$$

where r is the angle of rotation.

5. Fluctuations in concentration.

As has already been indicated a dilute disperse system may be regarded as obeying the ordinary gas laws. If we imagine a small volume of the disperse system as separated from the bulk of the solution it will contain at any instant a certain number of particles n. Since these particles are agitated by Brownian movement the number of particles in the small volume will alter from moment to moment but always maintaining a mean value of n over long periods of time. If at any instant the number in the small volume be n_i then the relative alteration from the mean value n will be

$$\delta = \frac{n_i - n}{n}.$$

Or the mean value of these fluctuations in concentration will be

$$\bar{\delta} = \left(\frac{n_i - n}{n}\right)_{\text{mean}}.$$

v. Smoluchowski has shown on the assumption of the validity of Boyle's law for such suspensions, that

$$\bar{\delta} = \sqrt{\frac{2}{\pi n}}$$

when n is large and when n is small

$$\bar{\delta} = \frac{2n^k e^{-n}}{k!}$$

where k is the next smallest whole number when n is not a whole number, and is equal to n when n is a whole number.

If Boyle's law does not hold exactly, the above equations suffer the following transformations.

For large values of n, $\delta = \sqrt{\frac{2}{\pi n} \cdot \frac{\beta}{\beta_0}}$; for small values of n, $\delta = \frac{2n^k e^{-n}}{k!} \sqrt{\frac{\beta}{\beta_0}}$, where $\frac{\beta}{\beta_0} = \frac{RT}{v^2 \left(\frac{RT}{[v-b]^2} - \frac{2a}{v^3} \right)}$.

The probability of the presence of n_i molecules being present inside the small element of volume will be

$$\frac{n^{n_i} e^{-n}}{n_i!}.$$

6. Experimental verification.

On the assumption that the particles of a suspension diffuse at a rate dependent on the concentration gradient in the solution in a manner analogous to the molecules of a soluble solute the diffusion coefficient is given by the expression

$$D = \frac{RT}{6\pi \eta r N}.$$

This relationship permits of experimental verification by direct observation of the diffusion coefficient and the measurement of the radius of the particle. Svedberg (*Zeit. Phys. Chem.* LXVII. 105, 1907; *Archiv f. Kemi, etc., K. Svenska Vetensk. Akad. Stockholm*, B, IV. 12, 1911) employed colloidal gold prepared by reduction with phosphorus according to the directions of Faraday and Zsigmondy.

The density of the water employed as diffusion medium was raised by the addition of urea in order that the gold suspension could be run under a column of water without undue disturbance so as to obtain a uniform level surface of separation.

As a result of a series of experiments the following results were obtained.

T	η	D obs.	r calc. in $\mu\mu$	r obs. (by Zsigmondy)
(i) 284·7	0·012	0·27	0·6	*ca.* 0·5
(ii) 286·62	0·01209	0·117	1·29	1·33 (direct observation)

If the motion of one particle be observed it will oscillate about a mean position, the actual motion being naturally zig-zag, returning

after a comparatively long time interval very nearly to its original *position. The determination of the displacement of* a *particle in* a given time interval will thus vary with the interval chosen; from the relationship

$$\bar{x}^2 = \frac{RT}{3N\pi\eta r} \cdot t$$

the velocities for different time intervals will evidently increase as the time interval diminishes and at a rate proportional to the inverse square root of the time interval or $v^2 t$ = constant.

Likewise the displacement in a given time interval, i.e. for constant values of t, should vary both as $\frac{1}{\sqrt{r}}$, and $\sqrt{\frac{T}{\eta}}$.

Confirmation of these expected relationships have been obtained by Chaudesaignes (*C.R.* CXLVII. 1044, 1908), Perrin, Exner, and others.

With *gamboge particles* $1{\cdot}065 \times 10^{-5}$ *cm. in radius it was found* by examination of the motion of fifty particles at thirty second intervals that each moved on the average:

in	30 seconds	6·7	microns
„	60	„	9·3	„
„	90	„	11·8	„
„	120	„	13·95	„

whilst the square roots of the times are proportional to the numbers 6·7, 9·46, 11·6 and 13·4.

Svedberg obtained the following values for the displacement of gold particles over varying time periods, confirming the anticipated relationship $\bar{x} = \kappa\sqrt{t}$.

(*a*)

t in secs.	$\bar{x}$ in μ	$\bar{x}$ in μ calc.
1	1·2	—
2	1·6	1·7
3	2·0	2·0
4	2·4	2·4
5	2·5	2·8

(*b*)

t in secs.	$\bar{x}$ obs.	$\bar{x}$ calc.
1	4·0	—
2	5·4	5·7
3	6·2	6·9
4	7·8	8·0

For particles of a radius $r = 22\mu\mu$ the absolute displacements were calculated with the aid of Einstein's equation and compared

with those determined with the aid of the ultramicroscope. H
obtained

t in secs.	$\bar{x}$ in μ calc.	$\bar{x}$ in μ obs.	difference
1	4·3	4·1	+0·2
2	5·8	5·8	—
3	6·6	7·6	−1·0
4	8·3	8·2	+0·1

By observing the velocities of particles of radii 5×10^{-5} an $2{\cdot}13 \times 10^{-5}$ cms. respectively for equal time intervals the square o the velocities were found to vary inversely as the radii, thus wit a *thirty second time interval the following data were obtained:*

t	$r \times 10^5$ cms.	$\bar{x}$ calc.	$\bar{x}$ obs.
30 seconds	2·13	3·40	3·60
	5·00	1·56	1·55

By determination of the velocities of particles in water at variou temperatures Exner (*loc. cit.*) was able to show the dependence o the velocity on the temperature and viscosity of the medium h found:

t	$r \times 10^5$ cms.	$T°$ C.	η	$\bar{x}$
0·14 seconds	4·5	21	·010	33·0
		71	·004	51·0

whence $\sqrt{\frac{T_1}{\eta_1}} : \sqrt{\frac{T_2}{\eta_2}} :: 1 : 1{\cdot}7$ and $\bar{x}_1 : \bar{x}_2 :: 1 : 1{\cdot}6$.

These experiments have been extended and confirmed by Seddi with the aid of a microphotographic camera to the case of sus pensions of cinnabar (*Phys. Zeit.* IX. 465, 1908).

Svedberg (*Die Existenz der Moleküle*, Leipzig, 1912) employe as observational method a thin flat cell through which the colloida solution was run at a slow and known rate. The particles viewe through a micrometer eyepiece are seen as curves of light movin with a given amplitude A and wave length λ. All the particles

however, cannot be regarded as possessing a motion of a purely oscillating character about the axis of the flowing stream and thus Svedberg's method of examination of the displacements $\bar{x}$ in given time intervals is liable to be somewhat inaccurate. Nevertheless, as the following data indicate, good agreement between the experimental figures and the theoretical expectations was obtained.

Dispersion medium	Platinum particles $r = 25\mu\mu$				
	T° C.	$\eta \times 10^3$	A in μ	$t \times 10^3$ secs.	$\frac{A^2\eta}{t}$
Acetone	18	3·2	6·2	16	7·80
Ethyl alcohol ...	19	4·6	3·9	14	5·04
Amyl acetate ...	18	5·9	2·9	13	3·74
Water	20	10·2	2·1	0·65	6·72
n-Propyl alcohol	20	22·6	1·3	0·45	8·90

It will be noted that the value of the expression $\frac{A^2\eta}{t}$ is approximately constant.

In Einstein's formula $\bar{x} = 4A$, hence the anticipated dependence of A^2 on the viscosity and time of amplitude is amply confirmed by experiment.

Svedberg has likewise examined v. Smoluchowski's equation for

GOLD SUSPENSION.

No. of particles per $384\mu^3 = 1·4$.

n_i	Fractional frequency of occurrence		
	obs.	calc.	difference
0	0·07	0·02	+0·05
1	0·08	0·08	+0
2	0·11	0·16	−0·05
3	0·13	0·20	−0·07
4	0·23	0·20	+0·03
5	0·19	0·15	+0·04
6	0·12	0·09	+0·03
7	0·04	0·05	−0·01
8	0·02	0·02	∓0
9	0·01	0·01	±0

$$n = 3·81$$

$$\frac{n_i - n}{n} = 0·418$$

$$\frac{2n^k e^{-n}}{k!} = 0·408$$

$$\frac{\beta}{\beta_0} = 1·024$$

the fluctuation in concentration of suspensions with the time, experimentally with the aid of a Siedentopf-Zsigmondy ultramicroscope. Two suspensions were employed, one a gold suspension of mean particle radius $29\mu\mu$, the other one of mercury of mean particle radius $71\mu\mu$. The data given above are typical of the results obtained.

MERCURY SUSPENSION.

No. of particles per $384\mu^3 = 0{\cdot}5$.

n_i	obs.	calc.	difference
0	0·07	0·05	+0·02
1	0·15	0·15	±0
2	0·21	0·23	−0·02
3	0·21	0·22	−0·01
4	0·16	0·17	−0·01
5	0·11	0·10	+0·01
6	0·04	0·05	−0·01
7	0·04	0·02	+0·02
8	0·01	0·01	±0

$$n = 2{\cdot}99$$

$$\frac{n_i - n}{n} = 0{\cdot}479$$

$$\frac{2n^k e^{-n}}{k!} = 0{\cdot}450$$

$$\frac{\beta}{\beta_0} = 1{\cdot}134$$

7. Electrolytic coagulation.

It bas been noted that for substances which do not yield ions in solution, such as charcoal, the charge is always produced by the preferential adsorption of an ion from the solution, e.g. the hydrogen ion. For substances which yield ions in solution, e.g. the hydroxides, it is evident that the charge can be accounted for by superficial ionisation (see Zsigmondy, *Kolloidchemie*; Wolfgang-Pauli, *Trans. Farad. Soc.* XVI. 6, 1921), e.g.:

$$\{Fe(OH)_3\}_x \rightarrow \{Fe(OH)_{3(x-1)}\, Fe(OH)_2\}^+ + OH',$$

or

$$\{H_2SiO_3\}_z \rightarrow \{(H_2SiO_3)_{z-1}\, HSiO_3\}' + H^{\cdot}.$$

In some cases also the charge may be attributed to the entrainment of impurities in the substance during its preparation, thus in the formation of arsenious sulphide from the oxide and hydrogen sulphide there is little doubt that the colloidal arsenious sulphide contains hydrogen sulphide which undergoing partial ionisation results in the formation of a negatively charged colloid

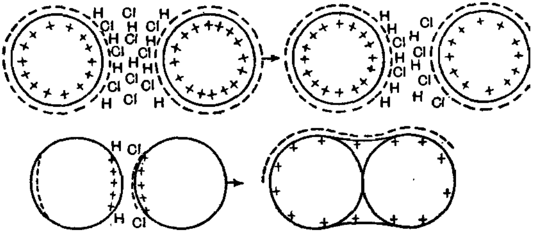
$$\begin{Bmatrix} As_2S_3xH_2S \\ H_2O \end{Bmatrix} \rightarrow \begin{Bmatrix} As_2S_3(x-1)H_2SHS \\ H_2O \end{Bmatrix}' + H^{\cdot} \rightarrow \begin{bmatrix} As_2S_3(x-1)H_2S \\ H_2O.S \end{bmatrix}'' + 2H^{\cdot}.$$

The coagulation and eventual precipitation of colloidal suspensions by electrolytes is the result of a series of reactions which in general cannot be isolated one from the other.

Coagulation, the result of approach, contact and coalescence of the particles of the suspensoid, is evidently hindered by any factor which may retard one of these three actions. The approach of one particle to another is brought about by the thermal or Brownian movement of the particles within the medium and factors such as low temperature, high viscosity of the medium or large particle size will *evidently diminish the rate of approach. When the* particles are in close proximity to one another, actual contact will be prevented if the particles possess electric charges similar in sign, due to the action of electrostatic repulsion. The particles will possess no net charge, i.e. their surface will be covered with the same number of cations and anions and will not repel one another at the isoelectric point when the capillary attraction can operate effectively (Hardy, *Proc. Roy. Soc.* LXVI. 110, 1900).

Actual electrostatic attraction may indeed take place between particles at the isoelectric point by processes which can be represented diagrammatically, as follows.

If the electric double layer is to some extent movable over the snrface of the particle we may imagine at the isoelectric point the effect of the mutual approach of two particles possessing each an equal number of cations and anions, e.g. $H^{\cdot}$ and Cl', in which the cations are most readily adsorbed in the following manner:



The normal distribution of ions in the double layer will be altered; in one particle the anions may be drawn to the exterior of the double layer, in the other the cations; whilst the ions of opposite sign will move away, thus the sides of the two particles in close proximity to one another will exhibit opposite polarity.

On the assumption of a somewhat mobile double layer, electrostatic attraction between particles may occur, due to this displacement effect, even if the total net charge be not zero, i.e. coagulation may take place before the isoelectric point is reached. The data of Zsigmondy on gold particles, and of Powis (*Zeit. Phys. Chem.* LXXXIX. 186, 1915) on oil particles, have indeed shown that the optimum point for precipitation is not actually at the isoelectric point, although in the case of gold, practically complete discharge of the double layer had to take place before coalescence.

Powis found in the case of oil emulsions, that a relatively large electrokinetic potential, $\zeta = 0{\cdot}040$ volt, did not prevent coagulation, an indication that the surface adsorbed layer is more mobile than for gold.

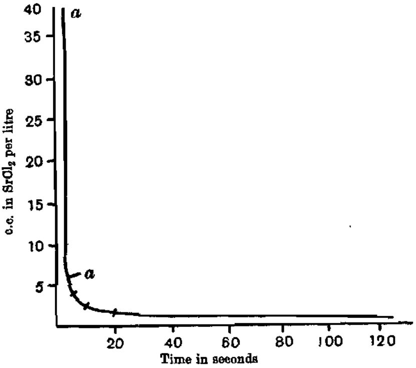
In addition to electric charge between particles other factors are in some cases operative in preventing actual contact, thus the medium may be strongly adsorbed by the surface, and the thin film may not readily be displaced on collision of the two neutral particles, in other cases a tough elastic film may be formed, possessing definite mechanical strength and necessitating a violent impact to ensure rupture.

Coalescence does not immediately follow after contact. Zsigmondy has noted, in the case of gold sols, under the ultramicroscope, that the small primary particles coalesce on contact to form secondary particles, that a primary will coalesce with a secondary, but two secondary particles do not coalesce.

The primary action of an electrolyte in the coagulation of a suspension is that of adsorption which is governed by the rate of diffusion. Subsequently the discharged or partially discharged primary particles coalesce, the colloid becomes more coarse, the secondary particles grow in number, and finally the colloid flocculates. If a coagulating electrolyte be added to a suspension in increasing concentrations, the velocity of aggregation first rises rapidly with the concentration, and then more slowly to a maximum

value. At this concentration we may assume that on every neutral approach of two particles to within a certain critical distance, coalescence occurs but in more dilute solutions only a certain fraction of the approaches are operative in producing coalescence.

The following curve obtained by Zsigmondy (*Kolloidchemie*, III. p. 67) on the effect of strontium chloride of different concentrations on the rate of conversion of a red into a blue colloidal gold indicates clearly the two regions of coagulation, one for high concentrations of electrolyte where the rate of precipitation is practically independent of the concentration and a region where, as has already been mentioned, every collision is not effective in producing coagulation and the rate of precipitation is greatly affected by the concentration of the added electrolyte.



Zsigmondy noted that the time of coagulation in the region of high concentrations (*a*—*a*) was not only independent of the concentration but also of the nature of the added electrolyte, being for the particular gold sol investigated a period of from 5 to 7 seconds. In this region we must assume that every collision between primary particles results in adherence and the rate of

adherence will thus be dependent on the magnitude of the Brownian movement causing the particles to diffuse within one another's spheres of attraction. v. Smoluchowski (*Physikal. Zeit.* XVII. 587, 1916; *Zeit. Phys. Chem.* XCII. 129, 1917) has calculated the rate of coagulation of a sol taking into consideration that not only do the primary amicrons but the secondary, tertiary and those particles of a higher state of aggregation continue to increase during the process.

If P_0 be the number of primary particles originally present in the sol and after a time t there be P_1, P_2, P_3 primary, secondary and tertiary particles present v. Smoluchowski showed that

$$\Sigma P = P_1 + P_2 + P_3 = \frac{P_0}{1 + \beta t},$$

where $\beta = 8\pi P_0 Dr$ in which $D =$ the diffusion coefficient and r the radius of the particle ($2r$ being taken as the mean distance apart of two particles when within one another's sphere of attraction).

Also
$$P_1 = \frac{P_0}{(1 + \beta t)^2},$$

$$P_2 = \frac{P_0 \beta t}{(1 + \beta t)^3},$$

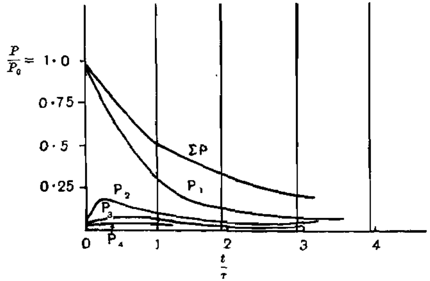
$$P_n = \frac{P_0 (\beta t)^{n-1}}{(1 + \beta t)^{n+1}}.$$

The half life of the suspension, i.e. the period which must elapse for the total number of particles to be reduced by coagulation to one half, the primary particles being simultaneously reduced to one quarter of their original number is given by

$$\tau = \frac{1}{\beta} = \frac{1}{8\pi Dr P_0}.$$

With the aid of the above expressions the number of particles of various complexities present in the solution after a time t expressed as a fraction or multiple of the half life τ can readily be calculated, these are graphed in the following curves.

v. Smoluchowski's formula has been tested both by an examination of the rate of decrease of the primary particles present in a gold suspension undergoing coagulation and also by counting the



rate of decrease of the total number of particles in similar suspensions.

The following data were obtained by Zsigmondy (*Zeit. Phys. Chem.* XCII. 600, 1918) for the rate of decrease of primary particles in a gold suspension undergoing coagulation:

$P_0 = 0{\cdot}27 \times 10^{10}$; radius of particle $24{\cdot}2 \times 10^{-7}$ cm.

t secs.	P_1 obs. (relative value)	$\frac{\beta}{2}$	P_1 cal.
0	1·97	—	1·97
3	1·56	(0·040)	1·76
20	1·02	0·0195	1·04
40	0·66	0·0183	0·64
40	0·76	(0·0153)	0·64
60	0·44	0·0187	0·44
80	0·49 (?)	(0·0126)	0·31

The mean radius of the sphere of action around each particle calculated from the observed rate of coagulation is $31{\cdot}82 \times 10^{-7}$ cm. or some one and a quarter times the actual radius of the particle.

Similar results have been obtained by Westgren and Reitstötter (*Zeit. Phys. Chem.* XCII. 750, 1918) with gold suspensions somewhat coarser than those employed by Zsigmondy and by Kruyt and von Arkel (*Rec. d. Trav. Chim. d. Pays-Bas,* XXXIX. 656, 1920) for selenium.

In the following table is given the rate of decrease of the total number of particles of a gold suspension undergoing coagulation:

t secs.	$\Sigma P \times 10^{-8}$	β cal.
0	2·69	—
60	2·34	0·149
120	2·25	·098
240	2·02	·083
420	1·69	·083
600	1·47	·083
900	1·36	·065
1370	1·20	·057

On the addition of small quantities of electrolyte all the amicrons are not discharged by ionic adsorption. Only those that are completely discharged or those for which the electrokinetic potential has been reduced below the critical maximum will actually adhere to one another on contact. We should thus with v. Smoluchowski (*loc. cit.*) replace the half life period $\tau = \frac{1}{8\pi DrP_0}$ by an expression $\tau = \frac{1}{8\pi DrP_0 x}$, where x is the number of successful collisions.

This expression for the slow coagulation has in fact been confirmed by Westgren (*Ark. f. Matem. Astron. och Fys.* XIII. 14, 1918) for coarse gold suspensions but the investigations by Paine (*Kolloidchem. Beihefte,* IV. 24, 1912) on copper suspensions of Miyazawa (*J.C.S.* Tokio, XXXIII. 1179, 1912); Ishizaka (*Zeit. Phys. Chem.* LXXXIII. 97, 1913; LXXXV. 398, 1913) and Gann (*Kolloidchem. Beihefte,* VIII. 65, 1916) on aluminium hydroxide and Lottermoser (*Koll. Zeit.* XV. 145, 1914) on tungstic acid and Wiegner (*Koll. Zeit.* VIII. 227, 1911) and Galecki (*Zeit. Anorg. Chem.* LXXIV. 174, 1912) on gold have shown that the rate of coagulation over the sensitive range of electrolyte concentration is not a simple reaction of the first order as postulated by the above considerations but behaves as if the reaction were autocatalytic in that the reaction velocity of coagulation can be expressed by means of an expression of the type

$$\frac{dx}{dt} = k(1 + bx)(1 - x).$$

As an example the following data obtained by Gann (*loc. cit.*) on the flocculation of an aluminium hydroxide sol with potassium chloride (60 millimol. KCl per litre) may be cited.

t min.	η	x	k
0	52·4	—	—
2	52·4	—	—
5	52·4	—	—
10	52·4	—	—
15	52·6	·0172	(·0017)
22	52·8	·0345	(·0018)
30	53·0	·0517	·0021
40	53·3	·0776	·0022
50	53·7	·1120	·0021
60	54·1	·1465	·0023
75	54·5	·1810	·0023
90	55·1	·2328	·0023
105	55·6	·2758	·0024
120	56·2	·3275	·0024
140	57·0	·3966	·0024
160	57·8	·4655	—
	$\eta_\infty = 64·0$		

The rate of coagulation of night blue examined by Biltz and Steiner (*Zeit. Phys. Chem.* LXXIII. 507, 1910) and of benzopurpurin (Biltz and v. Vegesack, *Zeit. Phys. Chem.* LXXIII. 500, 1910) likewise appear to conform reasonably closely to a reaction of the autocatalytic variety.

No satisfactory explanation for the autocatalytic behaviour of the flocculating suspension has as yet been advanced. The rates of coagulation have been determined in a variety of different ways, by ultramicroscopic counting in the case of gold, by alterations in the viscosity in the case of aluminium hydroxide, by the amount of precipitate separating in given times for the copper, and the increase in light scattering in the case of tungstic oxide. That all should indicate an autocatalytic action would appear to preclude any error being introduced by the methods employed for ascertaining the rate; we are thus forced to conclude that large particles formed by the aggregation of numerous amicrons act as nuclei on which further aggregation can occur more readily than on amicrons or small aggregates. When the suspension under examination is in motion the quantity of liquid streaming past and in the sphere

of influence of a large aggregate will naturally be greater than that flowing past a smaller particle and thus the number of possible contacts between the amicrons in the streaming liquid and the particles will increase rapidly with the size of the particle. This possible mode of mechanism for the autocatalytic nature of the process has been suggested by v. Smoluchowski (*Zeit. Phys. Chem.* XCII. 155, 1917). Apart from such mechanical effects, however, it would seem possible that the alteration in the electrokinetic potential of the aggregate on growth would lead to such an autocatalytic action as observed. We have already noted that coagulation may occur when this potential fall is not zero but slightly greater. If we imagine a particle with the critical electrokinetic potential it can only coalesce with an uncharged amicron. If the original charge be e and the radius of the particle r the potential of the particle will be $\frac{e}{Kr}$, where K is the S.I.C. of the medium. After coalescence the effective volume of the particle will be larger and its intrinsic potential consequently reduced to $\frac{e}{Kr'}$, where r' is obtained from the relationship

$$\tfrac{4}{3}\pi r'^3 = \tfrac{4}{3}\pi (r^3 + r_0^3).$$

If the diminution in intrinsic potential is accompanied by a corresponding decrease in the electrokinetic potential, the new aggregate will not be at the critical point but will be able to coalesce with another particle which possesses a slight electrokinetic potential. Thus aggregates will be built up which can react more readily than the small ones owing to a decrease in the interfacial potentials.

8. The Adsorption and Entrainment of Ions.

Colloidal suspensions and emulsions acquire their charge owing to preferential adsorption of cations or anions, thus a negative suspension or emulsion will be precipitated on the addition of an electrolyte containing a readily adsorbable cation, the added electrolyte however contains an anion as well, and tends to counteract the effect of the cation, hence the amounts of various electrolytes containing a common cation necessary to produce

coagulation will vary with the nature of the anion, as is instanced by the following data on the minimal amounts of electrolytes necessary to precipitate identical quantities of the same suspension.

Colloid	Sign	Minimal precipitating concentrations in millimols. per litre	
Platinum ...	–	NaCl 2·5	NaOH 130·00
$Fe(OH)_3$ ...	+	HCl 4·0	$BaCl_2$ 9·64

In the former case the sodion is the precipitating ion, in the latter the chloride, it is evident however that the hydroxyl ion is more readily adsorded by the platinum than the chloride necessitating a greatly increased concentration of the sodium hydroxide to effect precipitation.

A suspension or emulsion acquiring a positive charge owing to selective adsorption of a positive ion, e.g. $H^{\cdot}$ ion, will leave in the surrounding medium in the double layer an equal and opposite charge, e.g. a chloride ion; on the addition of a fresh electrolyte possessing a more readily adsorbable anion, e.g. Na_2SO_4, a reaction will occur:

$$\overbrace{\textit{Colloid}\ 2H^{\cdot}}+2Cl'+2Na^{\cdot}+SO_4'' \rightarrow \overbrace{\textit{Colloid}\ 2H^{\cdot}SO_4''}+2Na^{\cdot}+2Cl'.$$

The suspension or emulsion will be coagulated and the coagulum or precipitate will contain the coagulating anion in amount necessary to give the original suspension electric neutrality.

Crum (*Ann. Chim. Pharm.* LXXXIX. 156, 1854), analysing the coagulum produced by the addition of electrolytes to aluminium hydroxide, showed that the acid or salt necessary for coagulation was always present. Linder and Picton (*loc. cit.*) in their investigations on the precipitating power of various cations on *the negative arsenious sulphide suspension showed that the* precipitate always contained the cation, but never the anion of the precipitating electrolyte, e.g. $Ba^{\cdot\cdot}$, on the addition of barium chloride.

Whitney and Ober (*J.A.C.S.* XXIII. 842, 1901) on careful analysis of these precipitates found that the amounts of positive ion entrained

were proportional to their electrochemical equivalents, as indicated by the following table:

Ion	Mgm. ions adsorbed by 100 c.c. As_2S_3 sol.	
	obs.	cal.
Ba ...	7·6	(7·6)
Ca ...	2·0	2·2
Sr ...	3·9	4·9
K ...	3·6	4·3

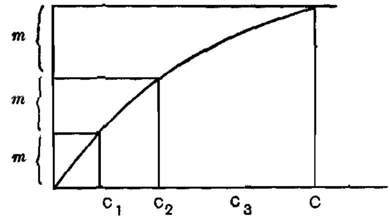
The precipitate on analysis gave the ratio Ba : $90As_2S_3$. The constancy of the ratio however depends entirely on the size and charge of the arsenious sulphide particles, since the reaction proceeds to the isoelectric point, i.e. electrical neutrality, and is therefore independent of any definite stoichiometric ratio of reactants.

Gann (*Kolloidchem. Beihefte*, VIII. 127, 1916) has likewise measured the adsorption of various precipitating anions by colloidal aluminium hydroxide and found that although the liminal concentrations necessary for precipitation are very different yet precipitation is caused on adsorption of equivalent concentrations as indicated by the following figures.

Anion	Liminal concentration millimols. per litre	Adsorbed quantity in milli-equivalents
Salicylate ...	8·00	0·30
Picrate	4·00	0·18
Oxalate	0·36	0·36
Ferricyanide ...	0·10	0·27
Ferrocyanide ...	0·08	0·29

In the adsorption of a monovalent, divalent and trivalent ion the amounts adsorbed to produce electrical neutrality will stand in the ratio $3m : 2m : m$, whilst if the adsorption is assumed to follow the Freundlich isotherm the bulk concentrations C_1, C_2, C_3 necessary to produce precipitation will evidently follow no regular order, but be dependent on the variables a and n of the isotherm expression. Thus on the addition of aluminium chloride to arsenious sulphide

some 50–60 °/₀ of the aluminium ions are adsorbed, whilst with monovalent cations only about 1 °/₀ is adsorbed.



Freundlich (*Kapillarchemie*, pp. 150–151; *Zeit. Phys. Chem.* LXXIII. 404, 1910) assumes that different ions are equally adsorbed at equal electrical concentrations. In the light of more recent investigation this assumption has been shown to be perfectly unwarranted.

In some cases adsorption of the ion resulting in precipitation may promote apparent hydrolysis, as instanced in the case of Fuller's earth (p. 187), thus if gum mastic suspension in water, a negative colloid, be floated on a solution of copper sulphate the copper ions will be adsorbed and the solution will be left feebly acid—a phenomenon noted by Spring (*Rec. d. Trav. Chim. d. Pays-Bas*, IV. 215, 1900).

The replacement of a positive ion in a negative colloid by another positive higher valent ion more readily adsorbable may result in electric neutralisation and consequent precipitation. Thus Duclaux (*Jour. Phys. Chim.* V. 29, 1907; *C.R.* CLIV. 1426, 1912) noted that negative suspensions of copper ferrocyanide prepared from the potassium salt always contained potassium and were precipitated in the usual way by other positive ions, e.g. $H^{\cdot}$, $Ba^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, the potassium ion however could afterwards be detected in the medium, indicating a replacement by the more readily adsorbed ion. The potassium was originally probably not part of the original complex ferrocyanide molecule, but adsorbed by the suspension from the solution. A similar displacement effect has been noticed by Pauli and Matula (*Kolloid. Zeit.* XXI. 49, 1917) in the case of sulphate ions displacing the less adsorbable chloride ions on ferric oxide.

9. Lyotropic series.

In the adsorption of electrolytes by charcoal it was noted that the organic ions were strongly adsorbed; in decreasing order of adsorptive power the hydrogen and hydroxyl followed by the other cations and anions in a regular series. The factors determining the position of the ion in this, the lyotropic series, were primarily the valency, and secondly its electropositive nature and mobility. The phenomenon of coagulation of suspensions gives a rough indication of the degree of adsorption of a particular ion, and the coagulation concentrations of various electrolytes for suspensions has been the object of many systematic investigations notably by Schulze (*Jour. f Prakt. Chem.* XXV. 431, 1883; XXVII. 370, 1883; XXXII. 390, 1884) Linder and Picton (*J.C.S.* LXI. LXVII. LXXI.), Freundlich (*Zeit. Phys. Chem.* LXXIII. LXXIX. LXXX. LXXXIII. LXXXV. LXXXVI.) Whetham (*Phil. Mag.* XLVIII. 474, 1899), Hardy (*Jour. of Physiol* XXXIII. 258, 1905) and others.

10. Hardy's Rule of Precipitation.

The effect of valency on precipitatory power is most marked, the polyvalent ions being much more effective than the monovalent ions. As a rough approximation the liminal concentrations, i.e. the concentrations in milligram ions, per litre necessary to cause coagulation vary with the valency in the proportion valency $1:2:3$, coagulative concentrations $1 : \frac{1}{x} : \frac{1}{x^2}$, where x is a constant approximately 30. The coagulative powers, i.e. the reciprocal of the coagulative concentrations of uni-, di-, and trivalent ions, should thus stand in the ratio $1:30:900$. The following ratios represent the averages of a number of readings by the various investigators:

Freundlich	1 : 104 : 810
Linder and Picton	1 : 63 : 863
Schulze	1 : 49 : 810

Evidently the valency relationship is by no means rigid, and in addition the various observations do not agree amongst themselves. It has already been noted that the process of coagulation is the result of a series of independent operations primarily dependent on an adsorptive process due to diffusion; the manner in which the

experiments are conducted thus effect the liminal concentrations observed. The addition of a strong solution of an electrolyte to a dilute suspension will produce local precipitation, whereas the addition of large quantities of dilute electrolyte to a concentrated suspension will not produce any effect although the final dilutions may be identical.

Again, it is extremely difficult to define precipitation. Small quantities of electrolyte will produce coalescence of the ultramicrons and the amicrons producing a coarser suspension before actual precipitation occurs; this again may only be partial.

The following method of comparing the precipitatory power of electrolytes has been found to give very uniform results.

The dilutions of electrolytes are so arranged that equal volumes of solution are added to equal volumes of the dispersion. The addition is performed rapidly, e.g. by adding 10 c.c. of electrolyte to 10 c.c. of suspension in test tubes. After thorough admixture the time elapsing to produce a standard degree of coarseness in the dispersion is noted. The standard can conveniently be made by the addition of small quantities of electrolyte and allowing the suspension to stand overnight. The degree of coarseness of the control is immaterial, provided precipitation does not take place. The concentration time curves of various electrolytes can readily be compared in this manner.

Burton and Bishop (*Jour. Phys. Chem.* June, 1922) and Kruyt (*Koll. Zeit.* XXII. 81, 1918; *Rec. d. Trav. Chim. d. Pays-Bas,* XXXIX. 656, 1920; XL. 249, 1921) have found that the ratio electrolyte : colloid is not the only governing factor in the production of coagulation; this ratio varies with the actual concentration of the suspension employed, and appears to obey a regular rule, which may be formulated as follows.

The ionic concentration necessary to produce coagulation varies with increasing concentration of the suspension, with univalent ions the ratio of electrolyte to suspension necessary increases, with trivalent ions it decreases, with divalent ions the ratio appears to be independent of the concentration.

The valency of the precipitating ion is however not the only factor operative, as is tacitly assumed in the law of precipitation already discussed. This fact is clearly brought out in the order of

adsorption of various ions on the surface of charcoal. A glance at the table indicates that in a definite series, such as the alkali metals or the halides (Pappada, *Koll. Zeit.* IV. 56, 1909) the electropositive nature of the element is an important factor.

11. Ionic mobility and adsorbing power.

There exists also a relationship between the adsorbing power and the ionic mobility, a point developed by Mukherjee (*Trans. Farad. Soc.* XVI. 103, 1921) embracing the following assumptions.

An ion adsorbed on the surface of a suspension will draw near to it an ion of opposite sign in the solution; these ions in the double layer are thus bound and can only escape if their kinetic energy exceeds a definite critical value W. If the chemically adsorbed ions have a valency n_1 and n_2 is the valency of the opposite charged ions in the liquid of dielectric constant K in contact with the solid and separated from the former by a distance x, we obtain

$$W = \frac{n_1 n_2 \epsilon^2}{xK}, \qquad \text{(i)}$$

where ϵ is the electronic charge.

The probability of an ion remaining fixed is given by $1 - e^{-\frac{W}{kT}}$, where k is the Boltzmann gas constant $= 1{\cdot}372 \times 10^{-16}$ erg/degree, T the absolute temperature. There will thus be at any definite temperature a number of free ions and ions bound to the double layer, the free ions will, as it were, form a second sheet in the double layer.

On the assumption that the double layer is of the order of 1 Å. (see p. 224) thick with a surface charge of $1 - 2 \times 10^4$ C.G.S. units, equivalent to 10^{13} monovalent ions per sq. cm., the mean distance between the ions is 3×10^{-6} cms., a distance extremely great compared with molecular dimensions. Mukherjee assumes in consequence that the neighbouring ions have but comparatively little effect on an oppositely charged ion at its position of minimum electrical energy.

The maximum amount of an ion of opposite sign that can be adsorbed per unit area is equivalent to the charge per unit area. If we denote the number adsorbed of valency n_1 by N, the maximum number of opposite sign that can be adsorbed N_m of valency n_2 is expressed by the relationship

$$N_m n_2 = N n_1. \qquad \text{(ii)}$$

If we denote by θ_1 the fraction of this maximum adsorbed when equilibrium has been reached in presence of ions of opposite sign in solution having a concentration c, then the rate of evaporation of these adsorbed ions must be equal to the number readsorbed in the same time. The rate of evaporation per unit surface is evidently

$$K_1 \theta_1 N_m e^{-\frac{W}{kT}}, \quad \text{.......................(iii)}$$

where K_1 is a constant and $N_m \theta_1$ the number of ions adsorbed per unit surface. The rate of adsorption depends on two factors: (*a*) the rate of collision of oppositely charged ions and (*b*) the number of places where adsorption is possible, that is, the spaces left by the free ions. This is given by

$$N - N_m \theta_1 = N\left(1 - \frac{n_1}{n_2}\theta_1\right). \quad \text{..............(iv)}$$

The rate of collision (*a*) is determined by the rate of diffusion of the ions to the surface, and by the electrostatic attraction between the ions. The former is equivalent to the action of a force equal to $\frac{RT}{N_0}$, whilst the intensity of the electrical field is proportional to the density of the charge on the surface and equal to

$$K_2'(1 - \theta_1) n_1 N n_2. \quad \text{.....................(v)}$$

Since N and n_1 are constants for the same surface we may write this expression as $K_2(1 - \theta_1) n$, where K_2 is a constant. In comparison with the enormous electrostatic field the diffusive force is negligible. Under these conditions the rate of collision is given by

$$K_3(1 - \theta_1) CUn_2, \quad \text{.....................(vi)}$$

where C is the ionic concentration in the liquid in contact with the surface and U the ionic mobility. The rate of adsorption being proportional to the rate of collision and the spaces available from equations (iv) and (vi) is given by

$$K_4 \left\{N\left(1 - \frac{n_1}{n_2}\theta_1\right)\right\} \{(1 - \theta_1) CUn_2\}.$$

Finally for equilibrium we obtain the relationship

$$K_1 \theta_1 N_m e^{-\frac{W}{kT}} = K_4 N\left(1 - \frac{n_1}{n_2}\theta_1\right)(1 - \theta_1) n_2 CU.$$

Since N, n_2, k and $e^{-\frac{W}{kT}}$ are constants for the same ion we obtain

$$\theta_1 = \kappa \frac{n_2}{n_1} C \left(1 - \frac{n_1}{n_2}\theta_1\right)(1 - \theta_1), \quad \ldots\ldots\ldots\ldots\ldots (a)$$

where

$$\kappa = \frac{K_4}{K_1} n_2 \overline{U} e^{-\frac{W}{kT}}.$$

Likewise for the fraction of the original charge not neutralised by adsorption we have

$$\theta_2 = 1 - \theta_1. \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (b)$$

Evidently the electrical adsorbability of an ion of opposite charge is dependent on the product nU or its valency and its mobility. Thus for a negative surface Mukherjee gives the following order of adsorption:

Th > Al > Ba > Sr > Ca > Mg > H > Cs > Rb > K > Na > Li

forming a lyotropic series, whilst for the anions the order should be

$$Br > NO_3 > SCN >$$
$$CO_3 > SO_4 > OH > I > Cl > COOH > F.$$

Mukherjee has extended his hypothesis to a consideration of the effects of electrolytes on electric endosmose, utilising the data of Elissafoff (*Zeit. Phys. Chem.* LXXIX. 385, 1912) (see p. 225).

On the assumption that at a glass-electrolyte interface hydroxyl ions are adsorbed, the fraction of the original charge neutralised by adsorption can be calculated from the above equations as follows. From (a) and (b)

$$\theta_1 = \kappa \frac{n_2}{n_1} C \left(1 - \frac{n_1}{n_2}\theta_1\right)(1 - \theta_1)$$

$$1 - \theta_2 = \kappa \frac{n_2}{n_1} C \left(\frac{n_2 - n_1}{n_2} + \frac{n_1}{n_2}\theta_2\right)\theta_2$$

$$= \left(\kappa C \frac{n_2 - n_1}{n_1}\right)\theta_2 + \kappa C \theta_2^2$$

or

$$\kappa C \theta_2^2 + \theta_2 \left(\kappa C \frac{n_2 - n_1}{n_1} + 1\right) - 1 = 0.$$

For hydroxyl ions $n_1 = 1$ and putting $n_2 = 1$ for the adsorption of an opposite charged monovalent ion we have

$$\kappa C \theta_2^2 + \theta_2 - 1 = 0.$$

For a divalent ion

$$\kappa C \theta_2^2 + \theta_2 (\kappa C + 1) - 1 = 0.$$

The following data calculated with the aid of these equations show a remarkably close agreement with those obtained by Elissafoff.

Electrolyte NaCl, $\kappa = \cdot 0076$.

Glass capillary concentration 10^{-6} gm. ion per litre	$50\theta_2$ obs.	$50\theta_2$ calc.
22·5	43	43·4
68	37	36·4
136	31	30·6
225	26	26·4
2240	8	10·6
4500	5	7·8

Electrolyte $BaCl_2$, $\kappa = \cdot 0163$.

Glass capillary concentration 10^{-6} gm. ion per litre	$50\theta_2$ obs.	$50\theta_2$ calc.
2·2	47	46·7
4·4	46	44
6	41	42
22	28	31·5
110	15	15

The two factors of valency and ionic mobility are however not the only ones to be considered in the phenomenon of adsorption, since the lyotropic series developed from these considerations alone should remain invariable in all cases of coagulation. This is far from being the case the order varying in a marked manner with the nature of the suspension. In addition, no adequate explanation of the abnormal position of the organic ions is forthcoming on this hypothesis. Bancroft (*Second Report on Colloid Chemistry*, p. 10, 1918; *Applied Colloid Chemistry*, p. 215) has made a careful summary of the series in order of precipitation, as observed by numerous investigators, which clearly indicate that chemical factors characteristic of suspension and electrolyte cannot be ignored. The following may be cited:

Colloid	*Order*	*Reference*
Sulphur ...	Ba, Sr > Ca > Al > Mg, Cs > Rb > K > Ni Cd, Zn > Na > NH_4 > Li > H	Odén, *Der Kolloide Schwefel*, 156, 1912
Platinum ...	Al, Pb > Ba > Ag > K, Na	Freundlich, *Kapillarchem.* 352, 1909
Silver ...	Al > Ba > Sr > Ca > H > Cs > Rb > K > Na > Li	Pappada, *Gaz. Chim. Ital.* XLII. 1, 263, 1912
Mastic ...	*Al > Hg_2 > H > Ba, Ca > Mg > Ag*	*Freundlich, Kapillarchem.* 367, 1907
Prussian Blue	Fe, Al, Cr > Ba, Cd > Sr, Ca > H > Cs > Rb > K > Na > Li	Pappada, *Zeit. Koll. Chem.* VI. 83, 1911
Hydrous ferric oxide	H > Ba > Mg > Li, Na, K	Pappada, *ibid.* IX. 233, 1911
Albumen ...	Th > Cu, Zn > Ca > Mg > Li > K Na > NH_4	Bancroft, *Applied Colloid Chem.* p. 218

Similar wide variations are found in the case of the anions when precipitating positive suspensions.

As an example of the great precipitating powers of the organic cations the following data given by Freundlich for the precipitation of colloidal arsenious sulphide are of interest.

Electrolyte	Liminal concentration millimols. per litre
NaCl	51·0
Guanidine nitrate	16·4
Strychnine nitrate ...	8·0
Aniline hydrochloride ...	2·52
Morphine hydrochloride ...	0·425
Neo-fuchsine	0·114

12. Sign reversal in suspensions.

There exists an equilibrium at the interface between a charged suspension and its solution consisting of a dynamic interchange of both cation and anion. If the suspension be positively charged the adsorption of the positive ion is greater than that of the negative at that particular concentration. On application of the Freundlich isotherm equation to each ion

$$x_c = a\,C_c^{\frac{1}{n}},$$

$$x_a = a'\,C_a^{\frac{1}{m}},$$

it is evident that if n and m are not identical on altering the concentration of the electrolyte, the amounts adsorbed of each ion will vary, thus permitting a change in the electrokinetic potential to take place. Bancroft (*Second Report*, p. 2) cites as example the addition of potassium bromide to silver nitrate. If one adds to a dilute solution of silver nitrate somewhat less than one equivalent of potassium bromide a positively charged colloidal solution of silver bromide is obtained the precipitate having adsorbed an excess of silver ions (and to a less extent potassium ions), over the nitrate ions in the solution. On adding exactly one equivalent the colloid is unstable since the electrokinetic potential is small; a slight excess of the potassium bromide results in the formation of a negatively charged colloidal solution of the silver bromide due to the adsorption of an excess of bromide ions (and to a less extent nitrate ions) over the potassium ions in solution. On increasing the concentration of the potassium bromide the adsorption of the potassium ions eventually equals the adsorption of the anions and precipitation ensues.

The diminution of charge and eventual reversal of sign produced by the addition of electrolytes is more marked in the case of the polyvalent ions, and has been carefully investigated by Burton (*The Physical Properties of Colloidal Solutions*, pp. 164–169) who in the case of a colloidal solution of copper obtained the following results:

Electrolyte	gm. ions per c.c. $\times 10^6$	Mobility at 15° C. $\times 10^5$	Electrolyte	gm. ions per c.c. $\times 10^6$	Mobility at 18° C. $\times 10^5$
KCl ...	0	+24·9	K_3PO_4 ...	0	+25·4
	17·0	+25·7		3·6	+21·5
	38·0	+26·2		7·2	+16·8
	74·0	+22·8		14·4	+ 3·4
	154·0	+18·7		21·6	− 4·8
				32·8	− 7·9
K_2SO_4 ...	0	+25·4	$K_3Fe(CN)_6$	0	+30·4
	7·7	+25·3		7·1	+14·0
	19·2	+24·0		14·3	+ 3·8
	38·4	+21·8		21·4	+ 1·0
	96·0	+14·4		28·6	− 1·5
	153·0	+ 0		42·8	− 9·1

13. Effect of non-electrolytes on suspensions.

Quincke noted (*Drude Ann.* VII. 57, 1902) that both chloroform and carbon disulphide rapidly effected the precipitation of china clay suspensions, an observation extended by Rona and György (*Biochem. Zeit.* XCVIII. 92, 1919) to many capillary active substances such as camphor and thymol. A similar precipitation by ethyl alcohol of platinum and charcoal suspensions has been observed by Billiter (*Zeit. Physiol. Chem.* XLV. 312, 1903) and Lehmann (*ibid.* XIV. 151, 1894), whilst W. Ostwald (*Grundriss der Kolloidchemie*, 471, 1909) noted that a silver suspension in water was precipitated on the addition of propyl alcohol. In general however although the addition of non-electrolytes to suspensions does not produce precipitation or coagulation yet the sensitiveness of the sols to precipitation by electrolytes is affected.

The alteration in sensitiveness of a suspension to electrolytes by the addition of a non-electrolyte was first noted by Blake (*Amer. Jour. of Sci.* XVI. 439, 1903) who observed that the quantity of potassium alum necessary to convert a red gold into a violet form had to be increased on the addition of ether to the suspension; the liminal concentration without ether was found to be ·00035 whilst in an aqueous solution saturated with ether ·00151 equivalent per litre were required.

Kruyt and van Duin (*Kolloidchemie Beihefte*, V. 269, 1914) have examined the alteration in sensitiveness to electrolytes of a suspension of arsenious sulphide to which various non-electrolytes had been added. They found that the influence of various non-electrolytes on the sensitiveness of the suspension ran parallel to the adsorption of the non-electrolytes from aqueous solution by powdered charcoal and that the most capillary active non-electrolyte exerted the greatest effect on the liminal concentration required for precipitation. Further it was observed that the addition of non-electrolytes lowered the liminal concentrations, i.e. increased the sensitiveness of the suspension to uni- and trivalent ions but increased the liminal concentrations, i.e. decreased the sensitiveness for divalent and tetravalent cations as will be noted from the following tables.

Isoamyl alcohol conc. millimols. per litre	Liminal concentrations of KCl	Ratio
0	53·5	—
44	48	0·90
66	46	0·86
88	42	0·79

Isoamyl alcohol conc. millimols. per litre	Liminal concentrations of $BaCl_2$	Ratio
0	1·075	—
66	1·16	1·01
78	1·32	1·23
92	1·38	1·27
Ethyl alcohol		
0	0·87	—
1560	0·97	1·12

Electrolytes	Liminal concentrations for water	Isoamyl alcohol concentration	Liminal concentrations	Ratio
KCl	53·5	88	42	0·79
NaCl	69	85	51	0·74
KNO_3	62	85	48	0·77
$\frac{1}{2}Na_2SO_4$	78	85	56	0·72
$BaCl_2$	1·07	92	1·38	1·29
$MgSO_4$	1·16	85	1·39	1·20
$ZnSO_4$	1·12	85	1·40	1·25
$AlK(SO_4)_2$	0·203	85	0·177	0·87
$\frac{1}{2}Ce_2(SO_4)_3$	0·166	85	0·149	0·90
$Th(NO_3)_4$	0·147	85	0·152	1·03
p-Chlor-aniline chloride	2·18	85	1·93	0·89
Benzidine nitrate ...	0·200	85	0·195	0·98

For a ferric hydroxide suspension they obtained an increase in sensitivity on the addition of both isoamyl alcohol and phenol to both univalent and divalent anions, whilst Freundlich and Rona (*Biochem. Zeit.* LXXXI. 87, 1917) have noted similar effects on this suspension on the addition of many other capillary active non-electrolytes such as the urethanes, camphor and thymol.

No adequate explanation for the effect of such non-electrolytes on the sensitiveness of the suspension is as yet forthcoming. It is

evident from the experimental data that the non-electrolyte is adsorbed by the particles and the sensitiveness is affected by such adsorption. W. Ostwald (*loc. cit.*) pointed out that the effect of adsorption of a non-electrolyte of low specific inductive capacity would be to lower the potential of the charged particle and thus a smaller adsorption of the precipitating ion would suffice to bring the potential within the region necessary for coagulation. Freundlich (*ibid.* p. 638) has noted that if this hypothesis be correct then since the cataphoric mobility of the particle is given by the expression (p. 230)

$$-v = \frac{KRC}{4\pi\eta}\zeta$$

a decrease in the value of K should be associated with a diminution in the velocity of cataphoresis. The following values were obtained for a ferric hydroxide sol on the addition of varying amounts of camphor and thymol.

	$v \times 10^4$ in cms. per sec., for 1 volt per cm.
Pure sol	0·4
5 millimols. per litre camphor	0·2
2·5 „ „ thymol	0·3

Although an alteration in the specific inductive capacity of the double layer may be effected by the selective adsorption of the non-electrolyte yet such an explanation is evidently by no means adequate; thus we find 1500 millimols. of ethyl alcohol as effective as 70 millimols. of isoamyl alcohol, whilst the dielectric capacities of water and the two alcohols stand in the ratio 81 : 20·8 : 5·7; again the anomalous behaviour of di- and tetravalent cations as noted by Kruyt and van Duin is not explicable on this hypothesis.

If the non-electrolytes are in fact selectively adsorbed it necessarily follows that the ions are displaced from the colloid surface; thus the non-electrolyte cuts down the adsorption of the ions of the added electrolyte. It has already been noted that the anions and cations of an added salt are not equally adsorbed and it is likely that the extent to which the ionic adsorption is cut down by the preferential adsorption of the non-electrolyte is not equal for each ion. In the case of the negative arsenious sulphide sol if the non-electrolyte cuts down the adsorption of the cation of an

added salt more than the anion, a decrease in sensitiveness will result; if the anion adsorption is preferentially cut down an increase in sensitiveness will naturally obtain.

This hypothesis (Rideal, *Proc. Camb. Phil. Soc.* XXIV. 101, 1924) has recently been tested experimentally by Weiser (*Jour. Phys. Chem.* XXXVIII. 1255, 1924) in which both the liminal concentrations required for precipitation and the actual adsorptions of the precipitating ions in the presence of various sensitising agents were determined.

14. Precipitation by protective colloids.

As has already been noted certain solvated colloids are readily adsorbed by colloidal suspensions such as gold or platinum and protect them, i.e. decrease their sensitiveness to precipitation by electrolytes. Experiments by Zsigmondy (*Gött. Nachrichten,* II. 177, 1916) and Gann (*Kolloidchem. Beihefte,* VIII. 252, 1916) have shown however that many of these "protective" colloids will precipitate gold suspensions when employed in small quantities. A comparison of the precipitating power of various protective colloids was made by the determination of the "precipitation number" U which is the weight in milligrams necessary to convert 10 c.c. of an acid red gold sol into the violet form. As typical of the U numbers obtained the following may be cited:

Substance	Inversion number
Glycocol	>80
Histidine	0·10—0·20
Peptone	0·04—0·06
Ereptone	0·02—0·04
Albumose	0·002—0·004
Gelatine	0·002—0·004
Aniline hydrochloride	8—12
p-Amidophenol hydrochloride	2—3
1-2-4-diamidophenol hydrochloride ...	0·10—0·20
p-Amidodiphenylamine hydrochloride ...	0·04—0·06
Tetramethyldiamidobenzophenone ...	0·03—0·05
Malachite green	0·0025—0·004
Methyl violet	0·002—0·003
Fuchsine	0·002—0·004
Casein	0·002—0·004
Haemoglobin	0·005—0·003

According to Gann (*loc. cit.*) the precipitative power of such

substances is dependent on the presence of an amino group and is thus constitutive.

In reality this assumption is not warranted as will be evident from the following considerations. We may regard amino acids consisting essentially of Zwitter ions in solution. At the isoelectric point the acid and basic dissociations of the Zwitter ion are equal whilst on the acid side of the isoelectric point we obtain positively charged cations on the basic side negatively charged anions. Thus gelatine of isoelectric point $P_H = 4{\cdot}7$ on the acid side supplies "gelatine H˙" ions, on the alkaline side furnishes "gelatinate" ions

COO –	←	– COO	←	COOH
|		|		|
NH_2OH		$-NH_2+$		$-NH_2+$
Alkaline		4·7		Acid

A solution of gelatine brought into contact with a colloidal solution of negatively charged gold less acid than P_H 4·7 will exert a protective action due to the adsorption both of the Zwitter ions and of the negatively charged gelatinate ions, but if brought into contact with gold more acid than P_H 4·7 the positive gelatine ions will be adsorbed, neutralise the charge and precipitate the gold. On further addition of acid gelatine however redispersion will result and we shall obtain a stable but positively charged gold sol.

Thus any amphoteric electrolyte may cause similar variations in precipitative power on each side of its isoelectric point. In the following table are given the isoelectric points of a few typical amphoteric electrolytes:

Amphoteric electrolyte	Isoelectric point
p-Amino benzoic acid ...	$7{\cdot}2 \times 10^{-3}$
Aspartic acid	$1{\cdot}1 \times 10^{-3}$
Trypsin	3×10^{-4}
Casein	2×10^{-5}
Gelatine	2×10^{-5}
Arsenious acid	$2{\cdot}4 \times 10^{-5}$
Tyrosin	$3{\cdot}9 \times 10^{-6}$
Denatured serum albumen ...	4×10^{-6}
Serum globulin	4×10^{-6}
Oxy-haemoglobin	$1{\cdot}8 \times 10^{-7}$
Alanin	$6{\cdot}1 \times 10^{-7}$
Glycocol	$8{\cdot}2 \times 10^{-7}$
Leucin	$8{\cdot}8 \times 10^{-7}$
Lysin	3×10^{-10}
Arginine	3×10^{-11}

The isoelectric point of an amphoteric electrolyte is likewise displaced by the addition of neutral salts as is instanced by the following values for chromated gelatine in the presence of various neutral salts.

Electrolyte	*Isoelectric point*
Na_2SO_4	$10^{-3 \cdot 6}$
$Na_2C_2O_4$	10^{-4}
NaCl	$10^{-4 \cdot 3}$
KCl	$10^{-4 \cdot 3}$
$BaCl_2$	$10^{-4 \cdot 8}$
$Co(NH_3)_6Cl_3$	$10^{-7 \cdot 0}$

Kermack and Wright (*Biochem. J.* XVII. 635, 1923) have shown that gelatine at a P_H of 4·7 exerts but little protective power on a negative gum benzoin sol, acid gelatine precipitates the colloid in small concentrations whilst alkaline gelatine protects it. Similar observations have been made by Zsigmondy on the effect of casein on gold, but its exact isoelectric point was not established.

CHAPTER IX

GELS AND HYDRATED COLLOIDS

1. Introduction.

In many cases of precipitation from solution the precipitate does not come down in a granular form but forms a jelly which is a rigid mass containing appreciable quantities of solvent and possessing properties akin to a solid. There is no marked definite transition point which distinguishes a granular precipitate from such a jelly or gel, thus we have seen that barium sulphate usually distinctly granular and microcrystalline may, under suitable conditions, be precipitated in a form in which the aggregates enclose a certain amount of water. The hydroxides of iron and copper precipitated at low temperatures appear as flocculent masses of macroscopical size and possessing a certain loose structure, whilst precipitation at high temperature results in the formation of granular precipitates. More gelatinous in character are the precipitates of alumina, silica and gelatine. The flocculent precipitates are evidently particles of a true gel which possesses but little mechanical resistance and are readily broken up by mechanical or thermal agitation. Gels can only be formed by process of precipitation either as a result of the interaction of two reagents or by cooling a solution containing the gel-forming material which possesses a positive temperature concentration coefficient.

2. The structure of gels.

Several theories have been proposed to explain the process of gel formation, and diverse views are held as to their actual structure. The conditions favourable to gel formation are experimentally determinable and have to be considered in relationship to the theories proposed (Svedberg, *Herstellung Kolloider Lösungen*, 1909; *Trans. Farad. Soc.* XVI. 3, 1921). The factors favourable to precipitation in the form of a gel are the following:

(1) High solvation of the particles.

(2) High number of particles per unit volume.

(3) Small difference in specific gravity between particles and liquid.

(4) No stirring of the system.

(5) Low temperatures which favour 1 and 4.

At one time it was considered that the gels were homogeneous or one-phase systems. Evidence in support of this hypothesis has been advanced by Pauli (*Kolloidchem. d. Eiweisskörper*), Katz (*Koll. Zeit.* IX. 1, 1917), Procter (*J.C.S.* CV. 303, 1914) and Loeb (*Jour. gen. Physiol.* III. 827, 1921; IV. 73, 97, 351, 1921–1922). The investigations of Procter and Loeb were confined chiefly to the chemical behaviour of gelatine (see p. 304) and to the phenomenon of swellings in this gel, a subject investigated systematically by Katz and extended by him to a variety of substances. Although an explanation of certain properties is afforded by the one-phase theory, there are many others, e.g. the actual mechanism of gelatinisation, the alteration of viscosity with the rate of shear, elastic fatigue, and others, which are not so readily interpreted on this basis. The ultimate test of the theory, however, is to be found in the optical resolution of the two phases, if they exist, by means of the microscope or ultra-microscope. Such a resolution into two phases is for many substances undergoing gelation by no means easy (Zsigmondy, *Kolloidchemie*, Ch. 62, 1920), e.g. for gelatine, starches, and the polypeptides, since not only may the refractive index of the substance differ but a slight extent from the environment, but owing to the high solvation of the particles visibility is still further diminished. Again since most gels possess a large number of particles per unit volume, light scattering in the Tyndall beam may be general over the field of vision and isolation thus rendered impossible.

Many gels however readily permit of optical resolution into two phases, and there is little doubt, owing to the general similarity between the various gels that all of them are in fact two-phase systems. The close similarity in properties such as diffusivity, refractive index and electrical conductivity of the sol and gel forms of substances like gelatine and the soaps (Graham, *Phil. Trans. Roy. Soc.* CLI. 183, 1861; Arrhenius, *Öfvers. Stockh. Akad.* VI. 121, 1885; Walpole, *Koll. Zeit.* XIII. 241, 1913; McBain, *J.C.S.* CXVII. 1806, 1920; *Proc. Roy. Soc.* A, XCVIII. 395, 1921) again support the hypothesis

that there is no abrupt change in physical state in the transition from the undoubtedly diphasic sol to the gel. The weight of experimental evidence is thus in general, although in some cases not conclusively, opposed to the one-phase theory of gelation, and a *two-phase structure is generally assumed.*

3. Two-phase theories of gel structure.

Various hypotheses have been advanced as to the nature of these separate phases which may conveniently be divided into two groups, those which favour an immiscible liquid-liquid system, and those which hold that gels consist of a solid-liquid system.

In the case of emulsions it was noted that there was no apparent limit to the ratio of the internal or disperse phase to the external or continuous phase. The disperse particles at first spherical under the action of surface tension could undergo close packing and assume a polyhedral or honeycomb structure. Under these conditions the external phase may be reduced to a mere skin forming the walls of the polyhedra. If this skin be a viscous liquid the emulsion will acquire a considerable mechanical strength and rigidity and may in effect possess solid properties forming an emulsion gel or grease. This two-phase theory of gels was first advanced by Bütschli (*Untersuchungen über Structuren*, 1898) from microscopic examination of a number of coarse gels in which signs of a cell wall were obtained, and was given support by the investigations of Van Bemmelen (*Die Adsorption*) on the vapour pressure of gels undergoing gradual desiccation confirming the existence of pores, presumably within a net-work. The two-phase liquid-liquid concept of gels was likewise advanced by Wo. Ostwald (*Pflüger's Archiv*, CIX. 277, 1905, CXI. 581, 1906) who assumed that a gelatine gel, for example, consisted of a solution of gelatine in water in a *solution of water in gelatine*, the two liquids possessing a definite interfacial surface tension. If the two liquids are perfectly homogeneous these gels would differ from the emulsion gels only in that the latter possess a third substance which goes to the interface diminishing the interfacial surface tension, whilst in these no such extraneous stabilising agent is present. In a gelatine gel for example, on increasing the gelatine concentration in the water, the water in gelatine phase grows at the expense of the gelatine in

water, and the spherical particles of the discontinuous phase will grow both in number and in size. If the similarity between the emulsion gels or greases and these gels persists evidently the honeycomb structure will obtain as the final form of a rigid gel.

The honeycomb theory of gels rigidly assumes the existence not only of two phases but of a disperse and a continuous phase, the continuous phase forming a net-work. The gelatine gel however differs from a true emulsion gel in that there is no stabilising agent, i.e. since there is no film at the interface, two spheres of the water in gelatine phase in close proximity to one another should, instead of producing a mutual distortion and flattening of the spherical surface, actually coalesce, resulting in the formation of an interlacing system of two continuous phases, a view supported by Bancroft (*Applied Colloid Chemistry*, p. 242) who points out that with a still further increase in the gelatine content of the gel water may actually be dispersed in definite drops in the gelatine phase.

4. The solid-liquid theory of gel structure.

Hardy (*Proc. Roy. Soc.* A, LXVI. 95, 1900) adopted a somewhat different hypothesis, suggesting that, in the case of gelatine, the gelatine phase was not, as supposed by Ostwald and Bancroft, a highly viscous liquid, but actually a solid solution. The gel would thus consist of a solid solution of water in gelatine containing within it a disperse phase of gelatine in water. Support to this hypothesis has been given by Freundlich (*Kapillarchemie*), by Fischer (*Soaps and Proteins*, 1921) and by Anderson (*Zeit. Phys. Chem.* LXXXVIII. 191, 1914). The outstanding difficulty in these assumptions is that a dilute solution of gelatine certainly consists of two phases of which one is assumed to be either a viscous or a solid solution of water in gelatine, and the other one of gelatine in water; the former is present in small quantities and the liquid is mobile. The solid phase must therefore be the discontinuous phase. Yet on gelatinisation it is assumed that the viscous or solid phase is continuous; this necessitates an inversion of the phases during gel formation, a point of view negatived by the close similarity between the sols and the gels in their permeability to diffusion and electrical conductivity. Furthermore this inversion would appear to be somewhat difficult of experimental realisation

if the water in gelatine phase were actually a solid, as supposed by Hardy, but certainly possible with a viscous liquid.

These difficulties involved in the two-phase theory of gel formation on the assumptions of a continuous highly viscous or solid phase enclosing a liquid within its pores do not arise if the reverse be assumed to present a picture of gel formation, i.e. a continuous liquid phase enclosing the highly viscous or solid material as the discontinuous phase. In the case of the emulsion-gels or greases the rigidity of the system is created by the mechanical strength of the continuous phase, such a rigidity is not necessarily excluded if the continuous phase be liquid, for example a cadmium gel in alcohol (Svedberg, *Trans. Farad. Soc.* XVI. 55, 1921), but is somewhat improbable. The characteristic elasticity of such gels is furthermore somewhat difficult to explain if the property be due to a series of isolated spherical elastic particles embedded in a relatively non-compressible and inelastic medium.

5. Gel Fibrils.

These two characteristic qualities of the gels are best interpreted on the assumption that the disperse phase does not consist of isolated particles but that union between a number of these particles takes place to form relatively short fibrils or threads, which intersect one another to form a felt in the irregular meshes of which the mobile liquid phase penetrates. The fibrils in the case of gelatine would, according to Bancroft, consist of a viscous water in gelatine solution, and, according to Hardy, a solid solution of water in gelatine.

The fibrillar nature of gels was first tentatively suggested by Bütschli who at first thought that the threads noted under high magnification were sections of a cell wall. Similar fibrils have been noted for a great variety of gels, notably by Zsigmondy (*Phys. Zeit.* XIV. 1098, 1913; *Zeit. Anorg. Chem.* LXXI. 356, 1911), Bachmann (*ibid.* LXXIII. 125, 1911; LXXIX. 202, 1912), Barratt (*Trans. Farad. Soc.* XLIX. 16, 1920), McBain and others.

The fibrils are produced as the result of the partial coalescence of a disperse medium consisting of a highly viscous liquid or a solid solution. According to the solid-liquid theory the fibrils are produced by the coalescence of the dispersed sol in the form of

crystalline threads, i.e. that the fibrils themselves are crystalline in their nature. Doubtless the fibril crystals are highly hydrated, and the fibril may thus be considered to contain both dispersion medium and disperse gel forming material. Evidence is in fact available from the study of soap, gels and curds that the hydration of the fibrils may be varied affecting the properties of the system.

That the fibrils were definitely crystalline was suggested by Flade (*Zeit. Anorg. Chem.* LXXXII. 173, 1913) as a result of examination of the gel of barium malonate in methyl alcohol, a point of view supported later by Stübel (*Pflüg. Archiv*, CLVI. 361, 1914) and Howell (*American Jour. of Physiol.* XL. 526, 1916). The X-ray examination of a number of gels, including silica, stannic oxide and vegetable fibres, such as cellulose and ramie fibre, by Scherrer (*Nach. Ges. Wiss. Göttingen*, p. 96, 1918) has confirmed the presence of a crystalline structure in these gels. Gelatine on the other hand exhibited no crystalline interference lines, but was found to be amorphous.

The crystalline structure of the fibril is likewise supported by a study of the crystal habit of a number of substances which can with care be made to gel. Benzopurpurin and chrysophenone crystallise readily in rigid needle-like crystals. Gels can likewise be prepared from these substances in which long gelatinous needle-like crystals have been observed. Needle-like crystals can likewise be obtained from solutions of dibenzoyl cystine which undergoes gelation with great readiness (Gortner, *J.A.C.S.* XLIII. 2199, 1921). The crystals obtained from these substances are of varied character, occasionally short and relatively stiff, as is probably the case in nitrocellulose and in dibenzoyl cystine, and at other times long, thin and flexible, as in benzopurpurin and the product formed by the interaction of iodine and cholic acid. The thin, flexible crystals will readily pass through a filter paper, and, under the microscope, are in continuous agitation, performing a series of twisting and spiral movements as a result of Brownian bombardment. It appears likely that the nature of the crystal thus formed is the governing influence in the rigidity and elasticity of the resulting gel.

The X-ray examination evidently provides a ready classification of the gels into the crystalline and non-crystalline varieties, of which the most well known is gelatine.

6. The structure of gelatine.

Attempts have not been lacking to prove that all fibrils including those amorphous in the X-ray examination are actually crystalline.

Bradford (*Trans. Farad. Soc.* XLV. 16, 1921) has attempted to prepare crystalline gelatine, by utilising relatively dilute solutions of gelatine. According to von Weimarn's hypothesis (see p. 204) conditions favourable to the growth of crystals obtain in a solution of low viscosity and but a relatively small degree of supersaturation; by cooling a dilute solution of gelatine past the point of saturation extremely slowly it was hoped to obtain actual crystals. He obtained in a 0·4 °/$_0$ concentration globules or spherites of 0·1μ diameter. The ultramiscroscopic fibril of gelatine thus probably consists of a streptococcic chain of minute globules or spherites.

The structure of these spherites is uncertain; Bradford assumes that they consist of a regular crystalline growth formed by multiple twinning of minute crystals. Scherrer's examination of gold sols, however, has revealed the fact that the crystal interference lines are well developed when the particle contains as few as eighty molecules arranged in the cube lattice, a spherite of 0·1μ diameter would probably show crystalline properties even if excessive twinning has taken place.

The investigations of Lehmann (*Flüssige Krystalle*), Vorländer (*Krystallinisch flüssige Substanzen*), Bose (*Phys. Zeit.* IX. 708, 1908; X. 32, 230, 1909) and Manjuin (*C.R.* CLII. 1680, 1911) on liquid crystals such as para-azoxy anisol, some of which, e.g. bromphenanthrene sulphonic acid, are definitely colloidal, have shown that when these substances are immersed in a liquid in which they are insoluble there is a constant alternation between the liquid and the solid crystalline states at the melting point where the thermal agitation of the molecules just balances the cohesive power, the crystals frequently assuming the spherical form under the influence of surface tension. These swarms are definitely composed of minute crystals since they exhibit the property of double refraction and are actually visible under a powerful magnification, but do not show the X-ray interference lines of true crystal structure (Van

der Lingen, *Verh. d. Deutsch. Physik. Ges.* xv. 913, 1913), a phenomenon *explicable on the hypothesis of the existence of orientated* but unevenly spaced molecules.

Gelatine spherites may well consist of such minute crystals possessing orientated directions but not equally spaced from each other and the whole mass rendered spherical under the influence of surface tension.

7. Rigid and moist gels.

But little is known as to the influences which affect the growth of crystals in the fibrillar form. There are evidently two methods of growth for a short fibrillar crystal, it can grow either longer or broader. In the regular growth of crystallisation the two growth rates are commensurate with one another; for the fibril an elongated and slender crystal is necessary, the more inelastic and drier the gel so much coarser is the fibril, i.e. its axial growth rate relative to its longitudinal is greater. It will be noted that, in those cases where the chemical constitutions of the gel forming material have been determined, they are almost invariably long molecules, e.g. the higher fatty acids in the soaps, the amyloses in starch and amino acids in albumen. The long molecules have in addition frequently, as is the case also in liquid crystals, a reactive group at each end of the molecule and always at one end. It appears probable that the molecules permitting growth in échelon are those in which fibril formation and hence gelatinisation is possible.

In the case of dibenzoyl cystine the effect of substitution of various groups in the molecule on its properties of gelatinisation supports this hypothesis of growth in échelon.

The replacement of the unsaturated —S—S— linkage by a saturated linkage such as $-\underset{H_2}{C}-\underset{H_2}{C}-$ destroys the power of gelatinisation, the replacement of the electro-negative benzoyl group by a more electropositive group such as —*H* or $-CH_3CO$ likewise destroys this property, substitution by the *p*-chlor or *p*-nitro benzoyl, however, does not destroy it. On replacement of the hydrogen of the carboxyl by a more electropositive element, such as sodium, the property of gelatinisation is likewise lost.

A similar chain formation has been suggested by Pauli (*Trans.*

Farad. Soc. XIV. 10, 1921) *for the composition of the sols and gels* of the inorganic colloidal hydroxides, e.g. zirconia produced by the hydrolysis of zirconium oxychloride. By electropotentiometric measurements of the hydrogen and chlorine ion concentrations of sols formed by hydrolysis as well as freezing point, conductivity and transport number determinations he has shown that a series of salts are formed of the types:

$$\left[Zr(OH)_4 . Zr(OH)_4ZrOCl_2Zr\overset{++}{O}\right]\overset{--}{Cl_2},$$
$$\left[Zr(OH)_4 . ZrOCl_2Zr\overset{++}{O}\right]\overset{--}{Cl_2},$$
$$\left[Zr(OH)_4 . Zr\overset{++}{O}\right]\overset{--}{Cl_2},$$

as well as the complex zirconic acid $[Zr(OH)_4ZrOCl_2\overset{--}{Cl_2}]\overset{++}{H_2}$, whilst in a similar manner he was able to identify the following in the gel forming sols,

$$[x\,Fe(OH)_3\,y\,Fe^{\cdot\cdot}],$$
$$[Al(OH) . Cl_2 . Al(OH)_2Cl],$$
$$[2Al(OH)_3Al(OH)_2Cl] \text{ and } \left[x\,SnO\,y\,Sn\,\overset{--}{O_3}\right]\overset{++}{K_2}$$

8. The imbition of liquids by gels.

The ultramicroscopic examination of a gelatinising sol reveals the presence of very small particles termed ultramicrons, it is assumed on the fibrillar theory that the ultramicrons aggregate to invisible threads or fibrils. As the gelatinisation proceeds the fibrils thicken and lengthen and in many cases may actually be rendered visible by powerful magnification under the microscope. The fibrils are diffused at random in the form of a felt through the material and may, as we have noted, be markedly crystalline in the filamentous, somewhat flexible in the fibrillary and distinctly mobile and flexible in the streptrococcic forms visible under the microscope.

The characteristic properties of the gels are dependent on the nature of the fibrils, the more coarse the fibrils the more moist and elastic the gel, the finer the fibril the drier and more rigid the resultant gel; silica gel may be taken as representative of a dry rigid fine fibril gel and gelatine as that of the relatively coarse elastic type.

9. Rigid gels.

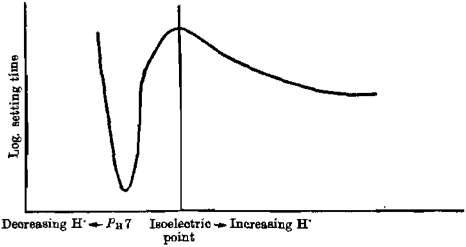
On drying a rigid gel the aqueous phase enmeshed in the felt-like fibrils begins to evaporate, the gel is sufficiently rigid as not to collapse as the interfibrillar spaces become emptied of water and filled with air. Such a gel will, on immersion in other solvents, e.g. toluene, benzene or alcohols, imbibe the liquid.

Coarse elastic gels, such as gelatine or rubber, on the other hand on drying begin to contract, the fibrils collapse or flow together as the interfibrillar water is removed. On immersion of the dried gel in various solvents imbition does not take place through the mechanical process of filling up empty pores, but only occurs if the liquid is actually adsorbed by the fibrils and is capable of redistending the gel. Imbition for the elastic gels is actually a case of adherence to the fibrils and is only caused by liquids possessing this property, e.g. water in the case of gelatine and benzene and similar nonpolar solvents in the case of rubber.

10. The properties of silica gel.

Silica may be taken as a typical representative of a number of gel forming hydroxides which may be either acidic or basic in their nature, e.g. tin, aluminium and iron, the acids of titanium, molybdenum and tungsten. Its preparation may readily be accomplished by the interaction of water glass (*ca.* 2 °/$_0$ SiO_2) and hydrochloric acid, although to obviate the subsequent removal of dialysable salts, hydrolysis of silicon tetrachloride or organo-silicon compounds has been suggested. The initial solution of ortho-silicic acid formed in this manner is unstable and is rapidly converted into the two-phase system; a sol of (Mylius and Groschuff, *Ber.* XXXVIII. 116, 1905) hydrated silica fibrils in a dilute solution of silicic acid. The sol thus formed is not very stable but slowly increases in viscosity as the fibrils link up with one another until a rigid gel is obtained. The conversion of sol into gel is not reversible and is affected by a number of factors, thus the rate of sol-gel transformation is very considerably increased on elevation of the temperature (Fleming, *Zeit. Phys. Chem.* XLI. 493, 1912) and also by the presence of various electrolytes. The sol particles of this relatively weak acid nndergo surface ionisation yielding a

negatively charged colloidal solution and the sensitivity of the setting time to hydrogen and hydroxyl ions is evident from the following curve.



The unstable sol evidently possess a maximum stability at the isoelectric point in contrast to the suspensions.

Very high concentrations of neutral salts are required to effect rapid gelatinisation of the silica sol (Hardy, *Zeit. Phys. Chem.* xxxiii. *391, 1900*; xxxiii. 11, 272, *1903*; Pappada, *Gaz. Chim. Ital.* xxxv. 1, 78, 1905).

Thus Pappada obtained the following values for the time in hours necessary to effect complete gelatinisation on the addition of 1 c.c. of electrolyte to 2 c.c. of a silica sol containing 6 gm. SiO_2 per litre.

	$\frac{SO_4}{2}$ (0·033*M*)	Cl	NO_3
Cs	36	37	57
Rb	82	72	90
K	106	122	116
Na	139	166	172
Li	188	216	280

The anion as is to be expected in the case of a negatively charged colloid evidently exerts but little effect. The sol-gel transition is generally examined by means of observation of the change in viscosity of the solution. The changes in viscosity as measured by the flow method in an Ostwald or similar apparatus differ as a rule

somewhat widely from the values obtained by the shearing process employing a rotating cylinder or oscillating pendulum. The determination of viscosity involves a rupture of a certain number of the fibrils when a shear method is employed whilst in the viscosometer the apparent viscosity will be widely different as the fibrils orientate themselves either in the stream line of the flow or at random directions. Such orientation of long and thih particles has been clearly observed in the case of the sol of vanadium pentoxide by Freundlich (*Physik. Zeit.* XVI. 413, 1913) and Kruyt (*Koll. Zeit.* XIX. 161, 1916). No satisfactory formula has as yet been proposed for the dependence of the viscosity of a sol on the molecular concentration of the sol forming material. Amongst those that have been proposed are those of Arrhenius (*Zeit. Phys. Chem.* I. 255, 1887) and Kendall (*Med. k. Vetenskap. Nobelinst.* XXI. 251, 1913)

$$\log \frac{\eta}{\eta_\infty} = KC,$$

where η_∞ is tbe viscosity of the medium and C the molecular concentration.

That of Hatschek has been found to possess a somewhat limited application to solutions of pseudo globulin and albumen, the formula proposed is $\frac{\eta_\infty}{\eta} = 1 - \sqrt[3]{\phi}$, where 100ϕ is the volume percentage of dissolved substance and its associated solvent (*Koll. Chem.* VIII. 34, 1911; XI. 284, 1912; XII. 238, 1913).

The formulae of Einstein

$$\frac{\eta}{\eta_\infty} = 1 + 2{\cdot}5\phi$$

and of Hess (*Koll. Zeit.* XXVII. 1, 1920)

$$\frac{\eta}{\eta_\infty} = \frac{1}{1 - a\phi} = 1 + a\phi + a^2\phi^2 \ldots$$

are evidently closely related to that of Arrhenius and Kendall.

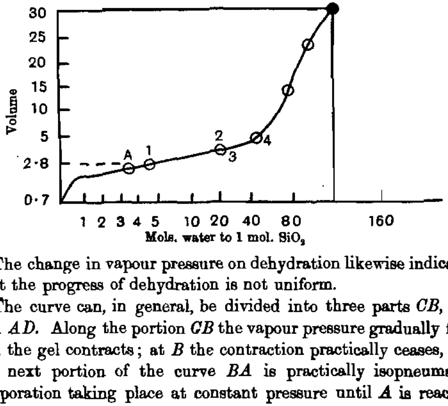
The behaviour of silica gel on desiccation and rewetting in water as well as in various organic liquids and gases has been investigated by Graham, Van Bemmelen $\{(CH_3\ COOH)\ (H_2O)\}$ (*Die Adsorption*, 1910), Bachmann (H_2O, CCl_3H, C_6H_6, $C_2H_2Br_4$, C_2H_5I) (*Zeit. Anorg. Chem.* LXXIX. 202, 1912), Anderson (C_6H_6, C_2H_5OH, H_2O) (*Zeit. Phys. Chem.* LXXXVIII. 191, 1914), Patrick (SO_2,

NH_3) (*J.A.C.S.* XLII. 946, 1920; XLIV. 1, 1922) and Daniells (NO_2) (*J. Ind. and Eng. Chem.* XV. 1173, 1923).

Gels containing over thirty mols. of water to one of silica are relatively mobile, those containing twenty mols. are stiff, with less water the gel becomes harder and can finally, with five or six mols. be ground up in a mortar to a fine powder.

On the progressive dehydration of a silica gel the gel rapidly contracts to a certain point, Van Bemmelen's "first inversion point" after which but little contraction takes place. On continued dehydration the clear gel suddenly becomes cloudy, then opaque, and finally loses its opacity again—Van Bemmelen's "second point" of inversion, when the water content has sunk to a ratio of one mol. of water to one of silica.

The volume change occurring on dehydration of a typical silica gel is shown in the following curve:

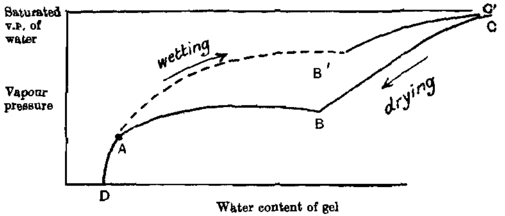


The change in vapour pressure on dehydration likewise indicates that the progress of dehydration is not uniform.

The curve can, in general, be divided into three parts *CB*, *BA* and *AD*. Along the portion *CB* the vapour pressure gradually falls and the gel contracts; at *B* the contraction practically ceases, and the next portion of the curve *BA* is practically isopneumatic, evaporation taking place at constant pressure until *A* is reached where a rapid change in pressure occurs.

Provided that desiccation of the gel is stopped at the point *D* on rewetting the dried gel the vapour pressure rises along the curve *DA*, i.e. the process of hydration and dehydration in this range is

perfectly reversible. As the water content increases the vapour pressure no longer follows the line *AB* but the vapour pressures of the rewetted gel are somewhat higher than those obtaining during the process of desiccation, and follow the line *AB'*. At *B'* a similar break *in the curve is obtained as noted during the period*



of desiccation and the vapour pressure rises rapidly along the line *B'C'*. The vapour pressure curves cannot be interpreted on the assumption of the existence of definite hydrates which should present a uniformly stepped curve, but as pointed out by Van Bemmelen (*Die Adsorption*) and Zsigmondy actually support the fibrillar theory of gels. Along the region *CB* the free water is removed from the gel and the fibrils contract until further contraction without decomposition of the fibrils is impossible. Along the region *BA* the gel remains practically constant in volume whilst the interfibrillar water is removed. That the line *BA* is very nearly parallel to the x axis is an indication that the fibrillary mesh is relatively uniform. If the interfibrillar water be removed some contraction and coalescence of the fibrils one with another takes place since the curve *AB* is not reversible the higher vapour pressure on the rewetting indicating a smaller mesh. Nevertheless this contraction is but small and the interfibrillar spaces left vacant by the water fill with air and the gel in consequence becomes opaque due to internal scattering of light at the multitudinous water-air interfaces until all the water is removed when the gel becomes clear again. At *A* the interfibrillar spaces are completely emptied and the vapour pressure drops rapidly on further desiccation when the adsorbed water on the gel fibrils is

removed. The removal of this water is a perfectly reversible process. After the adsorbed water is removed further dehydration of the gel results in disruption of the fibrils, which presumably consist of SiO_2H_2O and the gel structure is definitely destroyed.

The hypothesis that the curve *AB* represents a nearly, but not quite, reversible process of filling and emptying the interfibrillary spaces is, as has been noted, suggested by the fact that but a small change in gel volume occurs and that the changes in transparency occur, as would be anticipated. Experimental data by Bachmann (*Zeit. Anorg. Chem.* LXXIX. 202, 1912) and by Anderson (*Zeit. Phys. Chem.* LXXXVIII. 191, 1914) confirm this view.

Bachmann found that the volumes of various liquid imbibed by a silica gel within the region *AB* was approximately constant although the molecular ratio of imbibed liquid to silica might vary over a very considerable range.

A few of Bachmann's data calculated on the assumption that no contraction in the various liquids occurs on imbition are tabulated below:

Liquid	Interfibrillary volume in c.c. per gm. gel
Gel 1. Water	0·6210
Benzene	0·6270
Acetylene tetrabromide	0·6160
Gel 2. Chloroform (1) ...	0·2902
" (2) ...	0·2923
Ethyl iodide	0·2960

The interfibrillar spaces may be regarded as equivalent to a number of capillaries to which a circular cross-section may arbitrarily be assigned. At *B*, the largest of these capillaries are commencing to empty themselves by evaporation; at *A* the smallest of them are nearly empty. Anderson (*Zeit. Phys. Chem.* LXXXVIII. 191, 1914) has calculated these radii for a silica gel with the above assumptions from determinations of the vapour pressure with the aid of the equation

$$r = 2\sigma \frac{\rho_1}{\rho_2} \frac{1}{P \log \frac{P_1}{P}},$$

where ρ_1 and ρ_2 are the densities of the vapour and liquid respectively, P and P_1 the vapour pressures above a plane surface of the liquid and the gel.

Interfibrillar liquid	$r_{max.}$ in Å.	$r_{min.}$ in Å.
Water	27·4	13·7
Ethyl alcohol ...	25·8	12·1
Benzene ...	29·9	13·5

11. Gelatine and the Proteins.

The proteins consist essentially of amphoteric substances existing in equilibrium with both acidic and basic dissociation products of the type

$$P\begin{bmatrix}COO- \\ | \\ NH_2OH\end{bmatrix}- \rightleftarrows OH'+P\begin{bmatrix}COO- \\ | \\ NH_2+\end{bmatrix}+H^{\cdot} \rightleftarrows P\begin{bmatrix}COOH \\ | \\ NH_2\end{bmatrix}+.$$

Some like casein, salt free globulin and acid albumin are not heavily solvated in solution and are thus readily precipitated at the isoelectric point in a manner similar to the suspensions already considered. Others, e.g. glutin, gelatine and natural albumin, are solvated like silica which at the isoelectric point are not necessarily precipitated being maintained in the sol form by the solvent. On removal of the stabilising water however by the addition of alcohol or neutral salts precipitation will occur and this most readily at the isoelectric point.

In an amphoteric substance the ratio of the electrically neutral particles to the total concentration is at a maximum at the isoelectric point as is evident from the following considerations.

If c_A, c_K and x be the concentration of the anionic, kationic and undissociated protein in a solution then

$$c_A\, C_H = k_a x,$$

$$c_K\, C_{OH} = k_b x,$$

where k_a and k_b are the acid and basic dissociation constants of the amphoteric protein molecule. If the total concentration be n then

$$x = n - c_A - c_K,$$

or $$x = n - \frac{k_a x}{C_H} - \frac{k_b x}{C_{OH}},$$

or $$\frac{n}{x} = 1 + \frac{k_a}{C_H} + \frac{k_b}{C_{OH}},$$

and $$\frac{x}{n} = \rho \text{ the fraction of neutral particles}$$
$$= \frac{1}{1 + \frac{k_a}{C_H} + \frac{k_b}{C_{OH}}}.$$

In water as dispersion medium $C_H C_{OH} = k_w$ or

$$\rho = \frac{1}{1 + \frac{k_a}{C_H} + \frac{k_b C_H}{k_w}},$$

ρ is evidently a maximum when

$$\frac{1}{\rho} = \chi = 1 + \frac{k_a}{C_{H^\cdot}} + \frac{k_b C_{H^\cdot}}{k_w}$$

is a minimum or when

$$\frac{d\chi}{dC_{H^\cdot}} = -\frac{k_a}{C_{H^\cdot}^2} + \frac{k_b}{k_w} = 0,$$

hence $$\frac{k_b}{k_w} = \frac{k_a}{C_{H^\cdot}^2},$$

or $$\frac{k_a}{k_b} = \frac{C_{H^\cdot}}{C_{OH}},$$

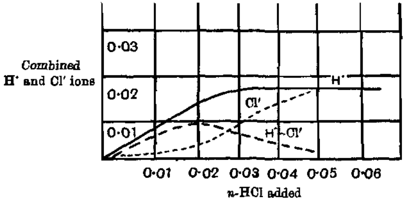
which is the isoelectric point.

On the progressive addition of an acid, e.g. hydrochloric acid to an isoelectric protein, e.g. albumin there will evidently be a progressive formation of the acid albumin AHCl. This will exist in equilibrium with its dissociated ions

$$AHCl \rightleftarrows AH^\cdot + Cl'.$$

The amount of undissociated albumin hydrochloride naturally increases with the addition of hydrochloric acid, thus if we plot the apparent fixation of both hydrogen and chlorine ions on the addition of hydrochloric acid to isoelectric albumin and also the difference between the hydrogen and chlorine ions adsorbed we shall obtain a well defined maximum for this difference at the point of maximum ionisation of the salt AHCl.

In the following curve are plotted the values obtained by Manabe and Matula (*Biochem. Zeit.* LII, 369, 1913) for ox serum albumin.

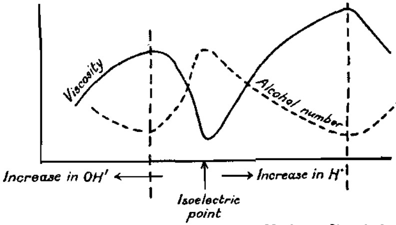


A similar point of maximum dissociation of the salt

$$NaA \rightleftarrows Na^{\cdot} + A'$$

will likewise be obtained on the addition of alkali to an isoelectric amphoteric protein.

Both isoelectric albumin and its undissociated acid and basic salts *are less solvated and imbibe less liquid than the ionised* form; thus the viscosity of an albumin solution will be least at the isoelectric point rising to more or less well defined maxima on each side, these maxima coinciding with the points of maximum dissociation of the two salts $\overset{+}{AH} \vdots Cl$ and $Na \,|\, \overset{-}{A}$ into the heavily hydrated ions. Again the precipitation of such hydrated or lyophilic colloids involves essentially two distinct processes, the *neutralisation of the electric charge by bringing the reaction of the* medium to the isoelectric point and the desolvation of the electrically neutral particles. It appears that both isoelectric proteins and the undissociated salts, e.g. AHCl and NaA, are less heavily solvated than the ionic forms $AH^{\cdot}$ or A'; thus the amount of alcohol required to precipitate a protein solution will evidently be least at the isoelectric point, greater on the progressive addition of alkali or acid, rising to more or less well defined maxima at the points of maximum dissociation of the two salts and sinking with the increase of the undissociated salts. The variation in these properties are diagrammatically represented in the following curves:



Maximum dissociation of salt
$NaA \rightleftharpoons Na^{\cdot} + A'$

Maximum dissociation of salt
$AHCl \rightleftharpoons AH^{\cdot} + Cl'$

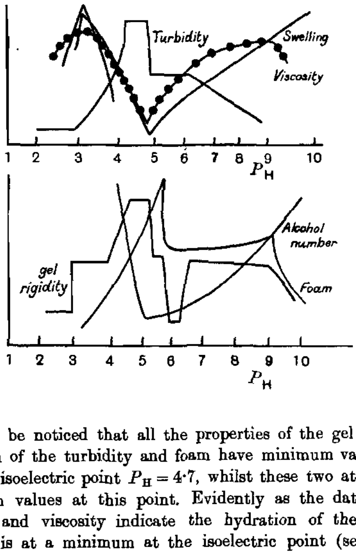
12. The properties of gelatine.

Commercial gelatine contains chiefly glutin and salts as impurities, the protein in the gelatine undergoes gradual hydrolysis to peptones and proteoses. Many of the physical characteristics of gelatine are dependent on the extent to which this hydrolysis has proceeded, e.g. its gelatinisation and muta-rotation (Bogue, *Chem. Met. Eng.* XXIII. 105, 1920; Smith, *J. Ind. and Eng. Chem.* XII. 878, 1920) and data obtained by various investigators on commercial and purified gelatine are consequently frequently at variance with one another.

The gel of gelatine differs from that of silica in that in the former the sol-gel transformation is reversible and not in the latter. The coalescence of the amicrons of gelatine to form streptococcic fibrils occurs at low temperatures, a process readily reversed by elevation of the temperature which decreases the amount of adsorbed water, increases the mobility of the fibrils, and permits of their rupture into smaller units. Gelatine is thus readily rendered more disperse by water.

Gelatine is an amphoteric electrolyte (Procter, *J.C.S.* CV. 313, 1914; Loeb, *Jour. Gen. Physiol.* I. 483, 551, 1918–1919; I. 39, 237, 363) having an isoelectric point at $P_H = 4{\cdot}7$–$5{\cdot}0$. On the alkaline side salts or gelatinates, e.g. calcium gelatinate, are formed, whilst on the acid side we obtain soluble gelatine salts, e.g. gelatine chloride, whilst isoelectric gelatine is apparently almost insoluble in water.

The influence of the hydrogen ion concentration on the various properties of the sol and gel forms of gelatine is most marked and has been investigated in detail by Loeb (*loc. cit.*) and Bogue (*J.A.C.S.* XLIV. 1349, 1922). A summary of the results of these investigations is given in the following curves representing the variation of the turbidity, viscosity, swelling, gel strength, foam and alcohol number with the P_H.



It will be noticed that all the properties of the gel with the exception of the turbidity and foam have minimum values at or near the isoelectric point $P_H = 4{\cdot}7$, whilst these two attain their maximum values at this point. Evidently as the data for the swelling and viscosity indicate the hydration of the gelatine particles is at a minimum at the isoelectric point (see Chiari, *Biochem. Zeit.* XXXIII. 167, 1911) where as indicated by the alcohol number it is most readily precipitated from solutions to form large aggregates to which the turbidity and the foam formation are due.

13. The swelling of gelatine.

The imbition of a dried gelatine by the addition of water is accompanied by a heat evolution and the exertion of a swelling pressure. Rodewald (*Zeit. Phys. Chem.* XXIV. 206, 1897) obtained the following values for the heat of wetting:

°/o H_2O	Calories per grm.
0·23	28·11
3·23	20·97
8·16	12·43
12·97	7·37
19·52	2·91

whilst the variation in the swelling pressure with the gelatine content was found to obey an expression of the type

$$P = ac^k,$$

where a and k were constants. The volume of the original gel together with that of the added water is always greater than that of the final gel. A not inconsiderable contraction occurs which is accompanied by the heat evolution mentioned above. It will be noted that as the water content rises the swelling pressure and the heat evolution decrease and at the same time the consistency of the gel becomes less. A large portion of the water is readily removed by application of pressure, whilst dilute gels will on standing undergo contraction accompanied by a coarsening of the fibrils and an exudation of the contained and adsorbed liquid, a phenomenon frequently termed syneresis.

As in the case of silica gel the water in a gelatine gel may be removed and replaced by other liquids such as alcohol, benzene or chloroform (Bütschli, *Über den Bau quellbarer Körper*, Göttingen, p. 22, 1896; Bachmann, *Zeit. Anorg. Chem.* C. 1, 1907). Gelatine, however, is relatively much more elastic than silica with the consequence that hysteresis is much more marked and the portion of the vapour pressure curve indicating the emptying of the interfibrillary spaces which should be parallel to the x axis (see p. 311) is extremely small denoting a progressive contraction of the mesh on removal of the containing fluid. Zsigmondy (*Kolloid-*

chemie, p. 373) has calculated the radius of the interfibrillary capillary as 70 Å., some three times larger than that for a similar silica gel.

The swelling of gelatine is, as has been noted, a minimum at the isoelectric point and increases on the addition of either acids or bases as well as on the addition of certain salts; thus with sodium salts the lyotropic series of decreasing swelling power is

$$CNS' > I' > Br' > NO_3' > ClO_3' > Cl' > H_2O > \text{acetate} > \text{citrate} > \text{tartrate} > SO_4''.$$

The swelling of such a gelatine is according to Procter (*J.C.S.* CV. 313, 1914; CIX. 307, 1916; *J. Amer. Leather Chem. Ass.* XI. 399, 1916) fully accounted for on the hypothesis that the conditions of equilibrium established between the gelatine in the interior of the thick fibrils and the interfibrillar liquid resemble those investigated by Donnan in his study on the behaviour of membranes separating a non-permeable ion from a solution containing membrane permeable ions.

We must assume that on the immersion of gelatine in a solution of a dilute acid, e.g. HCl, more acid than the isoelectric point $P_H = 4{\cdot}7$, the acid diffuses into the interior of the fibrils resulting in the establishment of the following equilibrium:

$$HCl \rightleftarrows \text{gelatine } HCl \rightleftarrows \text{isoelectric gelatine.}$$

Fibril	Interfibrillar liquid
$\overset{+}{GH}$ a	$H^{\cdot}$ x
$\overset{+}{H}$ b	Cl' x
Cl' c	

As we have already noted (p. 253) the product of the diffusible ion concentrations in the interior of the fibril bc and in the interfibrillar liquid x^2 will be equal. Now for all values of b and c, $bc > x^2$ unless $b = c$, there will thus be an excess of diffusible ions in the interior of the fibril over those in the interfibrillar liquid. This excess of diffusible ions in the interior will produce an osmotic pressure proportional to the difference in concentrations and cause the fibril to swell.

On swelling, an increase in surface energy of the fibril will result and equilibrium will obtain when this increase in surface energy

just balances the work done by the osmotic pressure in distension. It is of course possible to distend the fibrils beyond their elastic limits and thus cause disintegration of the gel.

The influence of neutral salts as well as of acids and bases on the swelling of gelatine which we have seen can be attributed to an apparent change in the solvation of the gel fibrils and may be interpreted in the light of Donnan's theory of the effect of a non-diffusible ion on the osmotic pressure differences between the two phases, is likewise to be noted in the alteration of the viscosity and alcohol precipitation values of protein solutions. From the considerations already advanced there should exist two well-defined maxima *in the viscosity and alcohol precipitation curves when these* properties are plotted as functions of the P_H, the maxima coinciding with the points of maximum dissociation of the salts

$$AHX \rightleftarrows AH^{\cdot} + X' \text{ and } HA \rightleftarrows H^{\cdot} + A'.$$

The studies of Pauli (*loc. cit.*) and his co-workers, however, have revealed the fact that isohydric solutions of different acids do not effect equal combination with the isoelectric protein; relatively more acetic acid for example being combined than hydrochloric acid in isohydric solutions. Again, both the actual position of these maxima as well as the magnitudes of the viscosities observed vary much with the nature of the acid employed. Thus the relatively weak oxalic acid appears to be a much stronger acid than sulphuric acid, whilst trichloracetic acid does not differ appreciably from acetic acid in its effect on the viscosity of albumin. It is probable that the degree of solvation of the protein molecules and of the protein salts must not be regarded as constant but that they vary both with the nature of the salt and in the presence of neutral salts which exert like alcohol a desolvating action more or less complete on the solvated isoelectric protein as well as on the undissociated protein salts.

In the case of gelatine, so far as this substance has been examined with care, the simple molecule can be regarded as a monacid base and a monobasic acid possessing but one potentially reactive —$COOH$ group and but one reactive —NH_2 group in its molecule. The other proteins appear to be relatively more complicated, thu on the progressive addition of strong acids to proteins such a

serum albumin a larger quantity of acid is taken up than on the addition of weak acids. Similar results are obtained with alkalis, the acid reacting power can further be enhanced by heat treatment with dilute acids (Adolf and Speigel, *Biochem. Zeit.* CIV. 175, 1920). These results are repeated in the case of alkalis, thus Pauli noted that the caseinate ion obtained on treating isoelectric casein with dilute soda was trivalent possessing a mobility of $v_{cas.} = 30{\cdot}1$, but on adding excess of alkali the combining capacity of casein increases to a maximum apparent valency of thirty. There is naturally associated with this increase in valency an increase in the ionic mobility. Pauli indeed (*loc. cit.* CIX.) advances arguments for the assumption of the following stages in the ionisation of casein on the progressive addition of alkali:

$$\text{Isoelectric casein} \rightarrow Na_3[(C''')\,C_x] \rightarrow Na_3(C''') \rightarrow Na_x\,C_x.$$

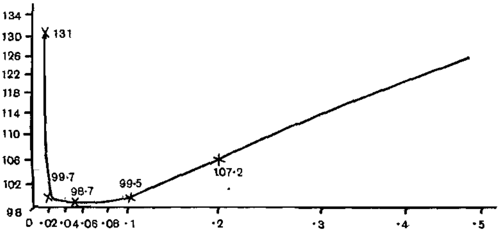
Whether the complex salt [Na_3C''' casein] must be regarded as a complex salt or an ionic micelle of the type investigated by McBain in his investigations on the soap solutions is not yet clearly established, whilst information on the acid and basic dissociation constants of the higher stages of dissociation of the complex protein is still lacking.

14. The Soaps.

The soaps consist of the sodium and potassium salts of the higher fatty acids possessing marked detergent powers. In alcohol they dissolve to form optically clear solutions in which the salts possess the normal molecular weights. In water, however, although the salts of the lower fatty acids which possess no detergent powers behave in a normal manner, yet as the length of hydrocarbon chain increases these solutions become increasingly abnormal both in their properties and behaviour. Sodium capronate ($C_5H_{11}COONa$) is the first salt to show any anomalous behaviour in that the elevation of the boiling point of aqueous solutions of the salt does not proceed indefinitely with increasing concentration but rises to a maximum and such strong solutions set to a gel on cooling. These abnormalities increase with the length of the hydrocarbon chain, the higher fatty acid salts showing but little elevation of the boiling point. Sodium laurate, however, is the first salt of the homologous series which may be said to possess all the properties

of a true soap. The examination of the molecular and ionic state of aqueous soap solutions by physico-chemical methods is a matter of some difficulty owing to the abnormally small values observed in such determinations as the molecular elevation of the boiling point (Krafft and Stern, *Ber.* XXVII. 1747, 1894) or the lowering of the vapour pressure (A. Smits, *Zeit. Phys. Chem.* XXXII. 1584, 1899; XXXIX. 385, 1902; XLV. 608, 1903), whilst the osmotic pressure methods are vitiated by the effects produced due to the appearance of a membrane equilibrium (Moore and Roaf, *Kolloid. Zeit.* XIII. 133, 1913). The most successful method of determining the molecular state with the aid of the direct determination of one of these colligative properties of solutions is by the lowering of the dew-point, a method developed by McBain and Salmon (*Proc. Roy. Soc.* March, 1920), by which the existence of molecular aggregates in aqueous solutions of the soaps was definitely established.

The examination of the electrolytic conductivity of soap solutions has, however, indicated that they are relatively good conductors and the conductivity concentration curve exhibits the interesting property of a definite minimum. The values for the specific conductivity of potassium palmitate are (McBain and Martin, *J.C.S.* CV. 957, 1914) plotted in the following curve.



The conductivity of the solution is not due to pronounced hydrolysis of the salt since determination of the hydroxylion concentration of the solutions have been made by McBain and Martin (*loc. cit.*) and McBain and Bolam (*J.C.S.* CXIII. 825, 1918), both by means of the hydrogen electrode and by the rate of catalysis of nitroso-

triacetonamine, the extent of hydrolysis is as observable from the following data relatively small.

POTASSIUM PALMITATE.

Soap conc. N	OH′ conc.	% hydrolysis
0·01	·0007	6·80
0·02	·0011	5·60
0·05	·0010	2·02
0·10	·0013	1·25
0·50	·0032	0·65
0·75	·0024	0·31
1·00	·0008	0·08

The product of hydrolysis is naturally an acid soap of varying composition. In any dilute solutions of sodium palmitate it approaches that of the sodium hydrogen soap $NaHP_2$. McBain and Taylor found that the acid soap at 90°C. had the composition HP.2NaP.

In order to account for the relatively high conductivity but low osmotic pressures and the low hydroxylion concentration of soap solutions, Bancroft assumed that the hydroxylions were adsorbed by the neutral colloidal potassium palmitate, this assumption was, however, proved to be incorrect by McBain who showed that on the addition of caustic soda no adsorption of the added hydroxylions took place. As an alternative explanation McBain suggested that the conductivity was due to the part of the soap which existed in the colloidal state, a colloidal ion. The colloidal soap ion differs from the ordinary charged colloidal particle in that not only is its mobility great but the equivalent conductivity is high, the conductance, in fact, being much greater than that of the simple ion of the fatty acid from which it is derived and comparable to that of a potassium ion. To account for the high mobility and equivalent conductivity of the colloidal ion in an electric field one must postulate that it possesses a relatively large charge for the number of molecules forming the aggregate and one must consider that the colloidal ion or ionic micelle (Nageli, *Pflanzenphysiologische Untersuchungen*, Zürich, 1858) is an aggregate of the ions of the fatty

acid the mobility of which will naturally be greater than that of the single ion since the resistance to motion of such an aggregate increases more slowly than does the charge. Such charged aggregate will, however, possess the small diffusibility of an ordinary colloid. There is a small but unmistakable difference between a potassium and a sodium palmitate solution which has led McBain to the assumption that the ionic micelle contains in addition to the ions some undissociated soap molecules together with water of solvation, the diminishing value of which as the concentration increases, accounting for the increase in the micelle mobility. Thus we ascribe to the ionic micelle of sodium palmitate the following composition

$$(NaP)_a\,(P')_b\,(H_2O)_c.$$

The value of b the number of palmitate ions in the micelle is at least ten. The examination of a solution of potassium oleate at a temperature of 0·18° C. by these methods has resulted in the following values for the concentrations of the various substances present.

Molality	Neutral colloid	Neutral salt	Ionic micelle	Oleate anion	Alkali ion
0·1	0·05—0·08	0·00—0·02	0·00—0·02	0·00—0·02	0·02
0·2	0·14—0·15	0·00—0·02	0·04—0·05	0·00—0·01	0·05
0·4	0·28—0·29	0·0	0·11	0·0	0·11
0·5	0·35—0·36	0·006	0·14	0·0	0·14
0·6	0·41—0·43	0·00—0·01	0·17—0·16	0·00—0·01	0·17

Aqueous soap solutions can be obtained in three distinct forms, the sol form containing the ionic micelle, a clear gel, and a white opaque solid the curd. The sol and gel forms of various soaps have beer examined by McBain and his co-workers and shown to differ onl in elasticity and rigidity, whilst the electrical conductivity, refractiv index, concentration of metallic ion and lowering of the vapou pressure are all identical, results to be anticipated on the fibrilla theory. The gel as we have seen is fibrillar in nature and the con version of a gel into a curd is brought about by the removal c soap from solutions in the form of relatively coarse fibres, a proces similar to crystallisation. The experiments of Laing and McBai

(*J.C.S.* CXVII. 1520, 1920) have shown, however, that a curd cannot be represented as a coarse gel felt of definite crystalline composition in equilibrium with a liquid phase since the conductivity of a concentrated curd is higher than that of a dilute one, and the solubility diminishes with the age of the curd. In the case of gelatine gels the evidence for a hydration of the fibril material is definite; in the proteins a variation in the degree of hydration of unionised and ionised protein molecules had to be assumed, whilst in soap gels the fibrils are undoubtedly solvated. The variation in the conductivity of curds may therefore reasonably be attributed to a difference in the degree of solvation of the fibrils, the more heavily solvated fibrils according to Laing and McBain's experiments being more insoluble and thus more stable. The less solvated fibrils can only become converted into the more stable solvated form by a process of solution and recrystallisation, a somewhat lengthy process extending over several months in solutions of such low diffusivity as soap.

The abnormality of the sodium soaps of the fatty acids of high molecular weight to form complexes in solution consisting of neutral colloid soap particles and of ionic micelle is to be attributed to the action of the long hydrocarbon chains, which are in themselves insoluble in water and tend to adhere to one another as the experiments of Langmuir (see p. 75) have indicated. The detergent action and emulsifying power of soaps is likewise due to this cause. If we insert in an organic material containing hydrocarbon chains sufficiently long so as to render their mutual lateral adherence great enough to overcome in part the disintegration due to the thermal agitation, polar groups of the type —COOX, —SO_3X, —$N(CH_3)_3I$, which are sufficiently strong to immerse the hydrocarbon chains, in water, we obtain substances possessing colloidal nature; detergent action, emulsifying powers, gel and curd forming properties will naturally be obtained (Reychler, *Koll. Zeit.* XII. 277, XIII. 252, 1913). Such solutions, if the non-polar portion of the molecule be too short or if too many polar groups be inserted or again if the polar medium water be replaced by one somewhat less polar such as alcohol, will no longer possess colloidal properties but will behave as true solutions.

15. The colloidal dyes.

Solutions of various dyes on their dispersion in water vary from the highly dispersed state, in which the molecular weight determined by the usual methods is found to be perfectly normal, to relatively coarse suspensions. The degree of dispersity of a dyestuff is partly constitutive in that the presence of polar or lyophilic *groups increases the dispersity. The dyestuffs are in this respect* comparable to the salts of the fatty acids where the relative magnitudes of the non-polar or lyophobic and polar or lyophilic portions of the molecule determine the state of aggregation in dispersion in water. They differ however from the soaps in that the solvation both of the molecules and of the neutral colloid and ionic micelle of the colloidal dyes is not so pronounced. In consequence the dyes are more susceptible to electrolytes which as in the case of the sols readily produce flocculation or a change in the aggregation of the particles.

Many such changes in aggregation are associated with a variation *in colour comparable to the colour change observed with gold* sols, thus the red tint of colloidal congo rubin (Ostwald, *Koll. Zeit.* XXIV. 61, 1919) becomes definitely purple on the addition of acids, bases or salts to the suspension, whilst the addition of electrolytes to true solutions of fuchsin render it colloidal. An alteration in the polarity of the polar group appears likewise to affect the dispersion. Thus phenolphthalein undergoes practically complete dispersion in alkaline solution, i.e. when present as its sodium salt, but is colloidal when present as the free acid. In the soaps we note also a change in solubility affected by similar means from the insoluble fatty acid to the relatively soluble sodium salt.

The *organic cations and anions are more strongly adsorbed than* even the polyvalent inorganic ions, thus precipitation of colloids or apparently complete adsorption by a charged surface (of opposite electric sign to that of the dye ion or ionic micelle) will occur down to very low concentrations of the dye. In addition as has already been observed, the somewhat lyophobic or sol-like character of the dyes, which renders them sensitive to electrolytes will permit of wide variations in the size of aggregate effecting precipitation or undergoing adsorption. Associated with this variation in size is a definite change in colour affecting the colour

of the dyed material. Non-colloidal dyes such as methylene blue, a positive ion, and eosine, an anion, may be utilised to precipitate colloids of opposite sign and will be markedly adsorbed both by charged suspensions and emulsions. Thus eosine is strongly adsorbed by silver halides stabilised with a positive charge, e.g. by excess of silver ions, but not by negatively charged halides, and can thus be utilised as an indicator.

Mutual precipitation of oppositely charged dye-stuffs is the basis of a number of volumetric processes of estimation; thus the evaluation of tannin solutions may be accomplished witb nigbt blue or of eosine with night blue.

The mechanism of dyeing (see *First Report on Colloid Chemistry*, *B. Ass.* 1917, for the complete résumé of the various theories) has received a great deal of attention and has led to the formulation of a variety of hypotheses sucb as the solid solution, the chemical, the adsorption and electrical hypothesis. A critical examination of the data on which these various alternative hypotheses rests would lead one to suppose that they are by no means irreconcilable with one another.

The process of dyeing appears to be an adsorption phenomenon; thus over a limited range in concentration the Nernst distribution law or the Freundlich isotherm will be obeyed, an observation confirmed by Georgievics (*Mitt. des K. K. Gewerbe-Museums in Wien*, pp. 165, 205, 349, 1904). Such adsorption compounds, however, are not similar to solid solutions as postulated by O. Witt, but due to true adsorption. As has already been noted the chief factor in promoting adsorption is the decrease in the free energy of the system, i.e. a lowering of the interfacial energy in accordance with the Gibbs' law; although solid skins of fuchsin, peptones and saponin may be formed at air-liquid and liquid-liquid interfaces it is improbable that any dyeing can result from such processes alone as the fastness or the formation of solid films is due to subsequent chemical changes occurring in the Gibbs' layer. The dyestuffs whether in true or colloidal solutions are all charged and are adsorbed by the material with the simultaneous neutralisation of their charge.

Cotton fibres are gel-like, usually negatively charged in water and readily adsorb basic colours, on increasing the negative surface

charge of cotton by the formation of oxy- or nitro-cellulose the affinity of the fibre for the basic colour is increased; the fibres of wool and silk are like the proteins amphoteric in their nature and can combine with both acid and basic dyes. Since the charge on gel fibrils is as we have seen localised at certain points along the fibril where the polar portions of the molecule are present the adsorption of a dyestuff at the point of saturation will be apparently stoichiometric, each polar group adsorbing its quota of dye. Thus in the adsorption of dyestuffs in true solution an apparent chemical action takes place as maintained by Knecht (*Jour. Soc. Dyes and Cols.* II. 242, 1904). If, however, the dye be colloidal the polar groups will still adsorb an electrical equivalent which will, however, be associated with a variable number of dye molecules dependent on the dispersity of the dye solution.

As has already been noted in other cases the distinction between adsorption compounds and chemical compounds is chiefly one of stability of union. In the process of dyeing evidently the adsorption formed by the specific adsorption of polar groups in the fibre for ions or ionic micelle of the dyestuff results in the formation of an adsorption compound which, however, will be relatively unstable and dyeing will not be fast. A closer union, however, results in the neutralisation of the electric charge on the dye ion and on the fibre and a process akin to coagulation takes place. The dye can now only be removed from the fibre by a strong peptising agent. Some apparently fast dyes may readily be peptised and removed from the fibre by replacing the water by an organic solvent which peptises the dye by adherence to the non-polar portion of its molecules.

16. Penetration in membranes.

An examination of the rate of penetration of a dyestuff, whether in true or colloidal solution, into a material exhibits many of the characteristics of the phenomena observed in diffusion in gels and plasmolysis through the membranes of cells (Overton and Meyer, *Studien über Narkose*, 1904; Hamburger, Gryns, *Pflüger's Archiv*). Charged ions or particles of the same sign as the fibrils penetrate relatively quickly, whilst those of opposite sign are precipitated during their course, and the rate of penetration is extremely small.

Substances, however, which are non-electrolytes as well as both ions and particles of the same sign as the gel fibrils penetrate at different speeds. The fibrils as we have noted are hydrated in solution and thus adsorb substances with polar groups whether ionised or not.

Substances possessing no polar group yet sufficiently soluble in water to permit of measurement of the rate of penetration will evidently *migrate* through the *interfibrillar* spaces unimpeded; but by insertion of polar groups in the molecule, the rate of penetration through the interfibrillar spaces is reduced by adsorption of the diffusing molecules in the adsorbed water layer round the fibrils. Such changes may conveniently be followed by observation of the migration rate of the boundary in transparent gels and by the rate of decrease of the osmotic pressure in the case of opaque gels or of membranes formed in porous partitions. Thus we find in decreasing rate of penetration as measured by the rapidity with which the initial high osmotic pressure of the solution decreases the following order for the substituted ureas:

$$CO\begin{matrix}\diagup NR_1R_2\\ \diagdown NR_1R_2\end{matrix},\quad CO\begin{matrix}\diagup NH_2\\ \diagdown NR_1R_2\end{matrix},\quad CO\begin{matrix}\diagup NH_2\\ \diagdown NR_1H\end{matrix},\quad CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix},$$

and on insertion of the following polar groups in a non-polar molecule a decreasing rate of penetration is observed as follows:

$$\text{amido-acid} > -COOH > C=O > CO.NH_2 > -OH > -CHO.$$

We find also that ethyl alcohol penetrates rapidly, glycerol more slowly, the tetroses extremely slowly and the pentoses and hexoses not at all.

Membranes themselves consisting of a porous colloidal net work may evidently undergo marked variation in interfibrillar or cross-section free space if the hydration of the membrane material be altered, thus affecting their permeability to various dissolved materials. As we have noted the *variation in the hydration* of the complex proteins is most marked as the hydrogen ion concentration is changed and it should thus be possible to effect alterations in membrane permeability by slight changes in the hydrogen ion concentration in the neighbourhood of the isoelectric point of the membrane.

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